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OXIDATION AND REDUCTION IN THE ANIMAL ORGANISM AND THE TOXIC ACTION OF POWERFUL OXIDIZING AND REDUCING SUBSTANCES.

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It occurred to one of us (Kastle) that those changes ordinarily included under the head of nitrification and denitrification could be brought about not only by certain micro-organisms but also by other life-forms, such as the higher plants and animals.

It was with this idea in mind that an experimental study of these changes was undertaken several months ago, and while the investigation has by no means been completed, some interesting results have already been reached, and in the present communication such of these will be considered as seem to throw light on the oxidation and reduction processes in the animal organism.

The Fate of Hyponitrites, Nitrites, and Nitrates in the Organism.

As part of the problem originally before us, it occurred to us to investigate the conduct and fate of hyponitrites, nitrites,

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and nitrates in the body of higher animals. The rabbit was chosen for the experiments, but in one experiment a cat was employed. It has been found that when rabbits are fed on a diet of boiled oats their urine shows no reaction for nitrite or nitrate. On a diet of succulent vegetables, however, nitrates can be readily detected in the urine by the diphenylamine reaction. Hence, during the period of experimentation and for some time previous thereto, the animals in use were kept on a diet of boiled oats. During the progress of the experiment the animal was confined in a wire cage so arranged that the urine could be collected in a flat porcelain dish. The urine was examined as soon as passed so as to avoid any secondary bacterial changes that might take place on standing. Diphenylamine was employed in testing for nitrates and Griess' sulphanilic acid reagent was used in testing for nitrites. In some instances nitrates were tested for by removing any nitrite present by boiling the solution to be tested with ammonium chloride, then reducing with zinc dust, filtering, and testing the filtrate for nitrite with Griess' reagent.

Rabbits of uniform weight and size were selected for the experiments, weighing on the average 1 kilogram.

Experiment 1, with Sodium Hyponitrite.—Five-tenths gram sodium hyponitrite in 3 cc. of water was injected into a rabbit subcutaneously. The animal showed some signs of pain for some time after the injection, due in all probability to the alkali resulting from the decomposition of the hyponitrite. The skin around the wound made by the needle remained moist for some time after the injection and the liquid which exuded therefrom was found to have an alkaline reaction. The urine which was passed at intervals after the administration of the hyponitrite was tested immediately, but no nitrite or nitrate could be detected. The animal soon regained its normal condition.

Experiment 2, with Hyponitrous Acid.—After an interval of several days the rabbit employed in Experiment 1 was given a subcutaneous injection of 3 cc. of N/10 hyponitrous acid. The acid employed was prepared immediately before the experiment by treating N/10 hydrochloric acid with an excess

of pure silver hyponitrite and filtering off the silver chloride. The animal urinated in five hours after the injection. The urine was tested for nitrites and nitrates. It was found to contain large amounts of nitrate but no nitrite. The urine of this rabbit was then tested as fast as the specimens could be obtained for five days following the injection. No evidence of nitrite was obtained at any time during this interval. The nitrate showed a steady and regular diminution in amount from day to day until at the end of the third day following the injection the urine failed to show the nitrate test. While apparently in perfect health, the animal died suddenly on the fifth day following the administration of the hyponitrite, whether from the effects of this substance or from other causes could not be determined.

Experiment 3, with Hyponitrous Acid.—A second rabbit was injected subcutaneously with 3 cc. of N/10 hyponitrous acid. The animal passed urine in fifteen minutes after the injection. This also gave a good test for nitrate with diphenylamine, and also by the other test which consisted in reducing with zinc dust and testing for nitrite with Griess' reagent. The urine did not give the slightest test for nitrites. This rabbit also died several days after the injection.

Experiment 4, with Nitrous Acid.—Tenth-normal nitrous acid was prepared by adding an excess of pure silver nitrite to a known amount of N/10 hydrochloric acid and filtering off the silver chloride. This operation was conducted at 0° C. in order to prevent the decomposition of the nitrous acid. Three cc. of the acid were injected subcutaneously into a young rabbit. Three hours after the injection the animal urinated. The urine was found to contain large amounts of nitrates and traces of nitrites. Neither of these substances could be detected in the urine of the animal prior to the injection of the nitrous acid.

Experiment 5, with Sodium Nitrite.—A young rabbit was injected subcutaneously with 3 cc. of a normal solution of pure sodium nitrite. The animal showed signs of pain and discomfort immediately and passed urine in ten minutes after

the injection. This urine gave no test for nitrite or nitrate. About thirty minutes after the injection the animal died suddenly, passing urine just a few moments before its death. In this specimen both nitrates and nitrites were found in abundance. The relative amounts of nitrate and nitrite were determined colorimetrically with the result that about three times as much nitrate as nitrite was found to be present.

Experiment 6, with N/2 Sodium Nitrite.—A young rabbit, weighing 1050 grams, received 3 cc. of a N/2 solution of sodium nitrite subcutaneously. The animal urinated five hours after the injection. This was found to contain both nitrates and nitrites in the ratio of five of the former to one of the latter. The animal continued in good health as long as he was under observation and at no time after the injection were any disturbances noted.

Experiment 7, with N/10 Sodium Nitrite.—A young rabbit was injected subcutaneously with 3 cc. of a N/10 solution of sodium nitrite. The animal urinated five hours after the injection. On examination it was found to contain considerable amounts of nitrate and only traces of nitrite. A specimen of the urine obtained from the animal before the injection showed neither nitrate nor nitrite.

Experiment 8, with N/100 Sodium Nitrite.—Three cc. of N/100 sodium nitrite was injected into a young rabbit. As in Experiment 7, the urine obtained from the animal after the injection gave tests both for nitrate and nitrite, the former in much the larger amount.

Experiment 9, with N/1000 Sodium Nitrite.—A young rabbit was injected subcutaneously with 3 cc. N/1000 sodium nitrite. The animal passed urine eight hours after the injection. It was found to contain nitrate but no nitrite.

Experiment 10, with 2N Sodium Nitrite on a Cat.—Three cc. of 2N sodium nitrite was injected subcutaneously into a full-grown cat. At first the nitrite seemed to exert a hypnotic effect and for some moments after the injection the animal remained in a somewhat dazed and sleepy condition. Then followed an abundant secretion of tears, and for twenty minutes the animal remained quiet, at the end of which time it was

observed to suddenly collapse. Violent convulsions then set in and these continued uninterruptedly until death occurred in fifteen minutes after the first collapse. During the period of convulsions there was an involuntary movement of the bowels and an abundant flow of saliva. Some of the saliva was collected and found to contain both nitrates and nitrites, the former in relative larger amount. A few moments after the injection the animal passed urine. It gave no test for nitrate nor nitrite. The post-mortem examination showed the abdominal and thoracic organs to be normal. The left ventricle of the heart was found to be stiff and full of blood. The blood itself was dark chocolate-brown in color. The bladder was found to be empty. Several of the organs, including the bladder, kidneys, and liver, were cut up into small pieces and allowed to stand for a few moments in contact with water containing small amounts of toluene as antiseptic. Both nitrate and nitrite were found in the solutions thus obtained, the former in excess.

Experiment 11, with Nitric Acid.—Three cc. of N/10 nitric acid were injected subcutaneously into a young rabbit. The animal urinated in one hour after the injection. The urine was found to be slightly alkaline in reaction and to contain nitrates, together with smaller amounts of nitrites. No toxic symptoms were observable.

Experiment 12, with Potassium Nitrate.—Three cc. of normal potassium nitrate were injected into a young rabbit. Before the injection, the urine of the animal contained neither nitrate nor nitrite. Two hours after the injection the animal passed urine which had a slightly acid reaction and was found to contain nitrates but no nitrites.

Experiment 13, with a Saturated Solution of Sodium Nitrate.—Six and five-tenths cc. of a saturated solution of sodium nitrate, containing five grams of the salt, were injected subcutaneously into a young rabbit, weighing 950 grams. The concentrated salt solution caused considerable pain and local irritation at first. This soon passed off, however, and the animal passed into a semi-comatose condition, which increased until several hours before death the animal had passed into a

deep coma. Death occurred eighteen hours after the injection. In this quantity the nitrate caused great thirst and acted as a diuretic, the animal passing urine five times in the first ten hours after the injection. The urine which was passed one hour after the injection was found to contain only nitrates, while that passed two hours after the injection contained also traces of nitrite. The amount of nitrite in the urine continually and regularly increased from this time on, until that passed ten hours after the injection gave excellent tests for nitrite. The urine was slightly alkaline in reaction at all times and contained large amounts of nitrate. The post-mortem showed the various organs to be normal, and the blood retained its bright-red color. The bladder was full of clear urine having a slightly acid reaction. It gave an excellent test for nitrites. Nitrites were also found in the blood and various organs, but in special abundance in the liver. In this connection it is interesting to note that Abelous and Gérard[1] found aqueous extracts of the liver and other organs of the horse to reduce nitrates to nitrites.

It is apparent, therefore, from these results that hyponitrous acid is oxidized to nitric acid in the animal organism. The fact that sodium hyponitrite escaped oxidation under similar conditions is probably to be explained by the fact that this salt is readily decomposed in aqueous solution into caustic soda and nitrous oxide. Then again, it seems to have been pretty well established that salts are more difficult to oxidize than the corresponding acid. It is further evident from our results that nitrous acid and nitrites are partially oxidized to nitrates in the body of higher animals, and also that nitric acid and nitrates are partially reduced to nitrites.[2] We have also observed that aqueous extracts of certain portions of some of the higher plants have also the power of

[1] Compt. rend., **129**, 56–58, 164–166 (1899).

[2] According to some writers the fate of nitrates in the body is somewhat uncertain. According to Weyl, in man the administration of 1 to 3 grams, by the mouth caused no increase in the amount of nitrate in the urine. It was supposed that the nitrate was completely reduced to ammonia or that it was finally excreted by the lungs as free nitrogen. Weyl's results have not been altogether confirmed by other observers and it is certain that when injected subcutaneously into lower animals the nitrate of the urine is greatly increased at the same time that some of it is reduced to nitrite and possibly to ammonia. (Virchow's Arch., **96**, 462, etc.)

changing nitrate to nitrite. Similar results have recently been obtained by Pozzi-Escot[1] in his study of the reductases. It would seem, therefore, that the power to effect those changes ordinarily included under the head of nitrification and denitrification is not confined to a comparatively few micro-organisms, but that these changes can be accomplished, less rapidly perhaps yet none the less certainly, by many if not by all of the higher life-forms. In their general bearing on oxidation and reduction phenomena in the organism our results have still a further significance. The fact that the higher animal can oxidize a nitrite and also reduce a nitrate would seem to indicate that oxidation and reduction processes in the organism tend towards the production and maintenance of a chemical equilibrium. That such is the case is seen not only in the conduct of nitrites and nitrates in the organism but also in the conduct of such compounds as aldehydes. We know now from the researches of Schmiedeberg,[2] Pohl,[3] Medwedew,[4] and Jacoby[5] that aldehydes, such as salicylic, benzoic, and formic aldehyde, are oxidized in the animal organism and also by the extracts of several organs, notably the liver, to the corresponding acid. On the other hand, that these substances are sometimes reduced in the organism is rendered evident by the fact that urochloral acid, a conjugation-product of trichlorethyl alcohol and glycuronic acid, appears in the urine after the administration of chloral. Evidently, therefore, chloral is reduced in the organism to trichlorethyl alcohol. Whether any of it is oxidized in the animal organism seems not to have been determined. The reason for this, however, is not far to seek. In the first place, there are no very delicate tests for its oxidation-product, trichloracetic acid, and in the second place, the salts of trichloracetic acid are readily decomposed in aqueous solution into chloroform and the bicarbonate of the metal,[6] so that it is more than likely that any trichloracetic acid resulting from the oxidation of the chloral

[1] This JOURNAL, **29**, 536–541.
[2] Arch. Exp. Path., **14**, 288–379.
[3] *Ibid.*, **14**, 38–65.
[4] Pflüger's Arch., **65**, 249.
[5] Virchow's Arch., **137**, 235.
[6] Ber. d. chem. Ges., **18**, 3336–3339.

would escape observation on this account. The decomposition of sodium formate into hydrogen and sodium bicarbonate by certain bacteria is a well-known instance of a biochemical reaction of this order.[1] Be all this as it may, we know that outside of the body chloral conducts itself like other aldehydes towards oxidizing agents and that, like all bodies of this class, it is a powerful reducing agent. We should, therefore, certainly expect the oxidation of this compound in the animal body as well as its reduction. Whether we shall ever be able to obtain experimental evidence of the products of its oxidation remains to be seen. Looking at oxidation and reduction processes in the organism from the standpoint of chemical equilibrium, it would seem that in the body of warm-blooded animals aldehydes would be simultaneously oxidized and reduced. This would account for the fact that in some cases acids, in other cases alcohols, have resulted from the introduction of aldehydes into the organism. If the first product of the oxidation is stable it, or some derivative thereof, will appear in the urine. Hence, as has been shown by Pohl,[2] formic acid appears in the urine when formic aldehyde has been administered to an animal. Or the first product of the oxidation of the aldehyde may be still further oxidized. For example, Pohl believes that formic acid is partly oxidized in the body to carbon dioxide and water. At the same time, however, that these oxidations are occurring, the reduction of the aldehyde is also being brought about, and in some instances at least the product of the reduction, an alcohol, or a conjugation-product thereof appears in the urine. Thus we observe that the appearance of urochloral acid follows the administration of chloral. On the other hand, if the alcohol resulting from the reduction of the aldehyde or its conjugation-product be not removed from the organism, it may also gradually suffer oxidation, and ultimately perhaps take the form of carbon dioxide and water. This would satisfactorily account for the very slow elimination of such substances as methyl alcohol from the body and would explain the apparent difficulty with which this substance is oxidized in the organ-

[1] J. Chem. Soc., Trans., 79, 386 (1901).

[2] For a résumé of Pohl's work see Reid Hunt: "Toxicity of Methyl Alcohol," Johns Hopkins Hospital Bulletin, 13, Nos. 137, 138.

ism. The tendency on the part of alcohols to react with fatty acids under the influence of lipase to form ethereal salts would also tend to retard the elimination of alcohol by the organism. In this connection Blyth[1] mentions the remarkable attraction which some tissues, notably the brain, have for ethyl alcohol.

The Toxic Action of Powerful Oxidizing and Reducing Substances.

On account of their great diversity in composition and mode of action it has proven extremely difficult to formulate a purely chemical theory of the action of poisons. The nearest approach to a general theory is that of Loew, according to which all substances which enter into combination with aldehyde and ketone groups are poisonous to life. According to this observer the labile proteid groups in protoplasm contain such aldehyde or ketone groups. In connection with our study of the conduct of hyponitrites, nitrites, and nitrates in the organism, we have come to be impressed with the large number of powerful oxidizing and reducing substances which act as poisons. The number of reducing substances, especially, which possess toxic properties, is indeed remarkable. The following may serve as examples of such compounds. The list of such might easily be extended:

Toxic oxidizing compounds.	Toxic reducing substances.
Nitrates	Nitrites
Chlorates	Hydrogen sulphide
Arsenates	Arsenites
Nitrobenzene	Aniline
Picric acid	Phosphorus
Chromates	Phosphine
Organic peroxides and peracids	Hydroxylamine
	Phenylhydrazine
	Benzene, toluene, turpentine, and other hydrocarbons
	Formic, acetic, and other aldehydes
	Methyl, ethyl, amyl, and other alcohols
	Pyrocatechol, resorcinol, hydroquinol, pyrogallol, etc.

[1] Blyth's "Poisons," Third Edition, p. 140.

No oxidizing compound has been included in the above list but such as is known to be reduced in the organism, and no reducing substance but such as is known to undergo oxidation in the body.

It is interesting to note in this connection that Binz and Schulz[1] have advanced the idea that the protoplasm of many tissues has the power to oxidize arsenious to arsenic acid and also the power to reduce arsenic acid to arsenious, as the result of which the cells are decomposed, fatty degeneration taking place. In this manner they account for the poisonous action of arsenic. It is not intended to convey by the ideas here advanced that the reducing or oxidizing power of a substance is the only property which determines its action as a poison, but rather that all oxidizing and reducing substances have at least one toxic property in common, *viz.*, that they upset the normal respiratory exchanges which occur in the organism, and thereby give rise to a series of disturbances, which may ultimately result in death. It is doubtful, for example, if all of the distressing symptoms which follow the administration of sodium nitrite can be ascribed solely to its action as a reducing agent. On the other hand, it certainly seems reasonable to conclude that this is an important element in its toxic effect, and that anything which like this substance so profoundly alters the oxyhaemoglobin of the blood must, regardless of its particular chemical constitution and specific effects, act as a poison. It is interesting to note in this connection that pharmacologists, among them Cushny,[2] look upon iodates as more poisonous than bromates, and bromates as more poisonous than chlorates. Now Rabuteau[3] has shown that iodates are completely reduced in the body, whereas bromates are reduced only to a slight extent and chlorates not at all. Later, Binz[4] found that potassium chlorate is rapidly reduced at body temperature by pus, yeast, fibrin, etc., so that it is more than probable that at least small

[1] Arch. Exp. Path. u. Pharm., 11, 131, 200; 13, 256; 14, 345; 18, 322; 36, 275; 38, 259; 41, 179.

[2] Cushny's "Pharmacology and Therapeutics," Third Edition, p. 529.

[3] Compt. rend., 74, 57.

[4] N. Rep. Pharm., 22, 733.

amounts of even the chlorate are reduced in the organism. It would seem, therefore, that among a series of analogous compounds the toxicity and power to effect oxidation stand in the same order.

In order to form some idea of the relative toxicity of sodium nitrite and hydroxylamine the following experiments on the rabbit were carried out.

Experiment 14, with N/2 Hydroxylamine Hydrochloride.—A rabbit weighing about 1 kilogram was injected with 3 cc. of a N/2 solution of Kahlbaum's pure hydroxylamine hydrochloride. The animal died twenty minutes after the injection. The internal organs were removed from the animal and placed in water under antiseptic conditions. No nitrite was found in the bladder, kidneys, liver, or heart, but by reducing with zinc dust and then testing with Griess' reagent nitrite was found in all of these organs, thereby indicating of course that all of them contained nitrate. Some of the blood also was dialyzed and found to contain both nitrite and nitrate,[1] the latter in much the larger quantity.

Experiment 15, with N/3 Hydroxylamine Hydrochloride.—A rabbit weighing 1100 grams was injected with 3 cc. N/3 hydroxylamine hydrochloride. The urine from this animal after the injection was found to contain nitrate but no nitrite. The animal died thirty hours after the injection.

Experiment 16, with N/5 Hydroxylamine Hydrochloride.—A rabbit weighing 1 kilogram was injected with 3 cc. N/5 hydroxylamine hydrochloride. The urine passed after the injection was found to contain nitrate and a trace of nitrite. No toxic effects were noted from this amount of the substance and the animal remained healthy as long as under observation.

[1] In this connection it should be observed that Raimondi and Bertoni (Gazzetta, 12, 195, 198, and 199–203) found that nitrites were present in the blood of animals after poisoning with hydroxylamine, and they have explained the poisonous action of hydroxylamine as really due to the nitrite resulting from it by oxidation. We also found nitrite in the blood of rabbits poisoned with hydroxylamine, but we have found considerably more nitrate than nitrite in the blood, tissues, and urine of such animals. We cannot, therefore, look upon the oxidation of hydroxylamine in the organism as stopping at the nitrite stage. The fact that sodium nitrite is itself oxidized in the organism to nitrate indicates that this cannot be the case.

Experiment 17, with N/3 Hydroxylamine.—A N/3 solution of hydroxylamine, the free base, was prepared by treating the hydrochloride with the required amount of caustic soda. A rabbit weighing a little over a kilogram was injected with 3 cc. of this solution. The urine obtained two hours after the injection was found to be slightly alkaline and to contain small amounts of nitrate but no nitrite. The animal died two days after the injection from the effects of the poison.

It will be seen from our results on sodium nitrite that 3 cc. of a normal solution of this compound, per kilogram body weight, was sufficient to kill a rabbit in thirty minutes, whereas 3 cc. of a half-normal solution of this salt had apparently no harmful effect, or at any rate the animal entirely recovered. The lethal dose of sodium nitrite, therefore, is not far from 3 cc. of the normal solution per kilogram body weight. On the other hand, from our results with hydroxylamine it would seem that 3 cc. of the N/3 solution represents the minimum lethal dose for the rabbit, per kilogram body weight. It would seem, therefore, that of two reducing agents that is the more toxic which possesses the greater capacity for oxygen, and in this connection it is interesting to note that in order to pass to nitrate, hydroxylamine requires three times as much oxygen as is required by sodium nitrite.

In conclusion, it is interesting to note that a great many pathogenic organisms are either anaerobic or facultative anaerobic, and that the growth of bacteria in an impoverished oxygen supply often results in the development of toxines. It has been shown further that diphtheria toxine is rapidly modified by air and sunlight, and that in the absence of air the diminution in toxic activity brought about by sunlight is comparatively slight.[1] It has also been observed by Pasteur[2] that on exposure to air cultures of the anthrax bacillus and the micrococcus of fowl cholera show a gradual loss of pathogenic power. This loss is, according to him, due to the action of oxygen. These and many other facts of kindred nature seem to indicate that lack of oxygen is favorable to the production of

[1] See also Woodhead's "Bacteria and Their Products," p. 141.
[2] Sternberg's "Bacteriology," p. 168.

poisonous compounds by the organism and that probably the toxines themselves belong to the class of reducing poisons.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, Sept., 1903.

Contributions from the Chemical Laboratory of Harvard College.

ON THE PREPARATION OF FORMIMINOETHYL ETHER.[1]

BY H. B. HILL AND O. F. BLACK.

The formiminoethyl ether, $NHCHOC_2H_5$, has become a reagent of some importance on account of its use in Claisen's process for making acetals,[2] but the only method of preparing it was that of its discoverer, Pinner,[3] which consisted in shaking a mixture of anhydrous prussic acid and absolute alcohol in the proportion of 1 molecule of each, diluted with absolute ether, with a little more than a molecule of hydrochloric acid gas in a freezing-mixture. This process is certainly undesirable because of the large quantity of anhydrous prussic acid which must be used, and also since it requires very careful manipulation and regulation of the temperature to prevent dangerous explosions.

In the hope of removing these disadvantages we have substituted mercuric cyanide for the prussic acid and have found that in this way a yield of 84 per cent of the double salt,

$$HClHNCHOC_2H_5HgCl_2,$$

can be obtained without difficulty, so that the preparation of the formiminoethyl ether becomes a simple and convenient operation. The details of the process follow:

Twenty grams of finely powdered mercuric cyanide and 21.6 grams of mercuric chloride were mixed in an Erlenmeyer flask with 7.3 grams of absolute alcohol diluted with several times its volume of absolute ether. The proportions give 2 molecules of the alcohol to each molecule of the cyanide. The flask was then immersed in ice-water and treated with dry hydrochloric acid gas, with frequent shaking, until the

[1] The work described in this paper was done under the supervision of Professor Hill, but the paper was written after his untimely death. C. L. J.

[2] Ber. d. chem. Ges., 31, 1010.

[3] *Ibid.*, 16, 354.

mercuric cyanide had gone into solution and the liquid fumed strongly. The mixture was then allowed to stand for half an hour, during which time the double salt crystallized out in colorless plates. These were filtered out on the pump and washed several times with anhydrous ether. The yield from 20 grams of mercuric cyanide was 51 grams of the crystalline salt, amounting to 84 per cent of that required by the theory, if all the cyanogen was converted into the salt. The double salt is comparatively stable and its formation was attended with no perceptible evolution of hydrocyanic acid.

A sample of the salt dried *in vacuo* over potassic hydrate and sulphuric acid gave the following results on analysis:

I. 0.5022 gram substance gave, on combustion, 0.1723 gram CO_2 and 0.0944 gram H_2O.

II. 0.4913 gram salt gave, by the Carius method, 0.5572 gram AgCl.

III. 0.4312 gram substance gave 0.4888 gram AgCl.

IV. 0.3082 gram substance gave 0.1880 gram HgS.

V. 0.3177 gram substance gave 0.1947 gram HgS.

	Calculated for $C_3H_3NOCl_2Hg$.	Found. I.	II.	III.	IV.	V.
C	9.46	9.35	....	....	....	....
H	2.10	2.09	....	....	....	....
Cl	27.99	....	28.04	28.02	....	....
Hg	52.55	....	....	....	52.58	52.82

The formula of the substance is therefore

$$HClHNCHOC_2H_2HgCl_2.$$

To prove that the substance is a salt of the formiminoethyl ether some of it was suspended in absolute ether and mixed with aniline, when a precipitate, probably a double chloride of mercury and aniline, was formed. The ethereal filtrate from this deposited, on evaporation, light-yellow needles, which, on recrystallization from dilute alcohol, melted at 135° to 137°, showing that they were the diphenylformaniline prepared by Pinner[1] by the action of aniline on the formiminoethyl ether.

It still remained to be proved that this mercuric salt could

[1] Ber. d. chem. Ges., 16, 358.

take the place of the chloride of formimino ether in Claisen's reaction. Accordingly, the following experiment was made: Fifty grams of the mercury salt of formiminoethyl ether were dissolved in absolute alcohol, using a little more than 2 molecules of alcohol to each molecule of the salt. In a short time the solution became full of white, silky needles, which were finally deposited in such quantity that the whole set to a hard mass. This, after standing for several days, was extracted with absolute ether and the extract submitted to fractional distillation. In this way 7.5 grams of a liquid were obtained, boiling at 145° to 147°, and therefore orthoformic ethyl ether, $HC(OC_2H_5)_3$. This reaction shows that the salt can be used in place of the chloride in preparing acetals according to Claisen's method, since this depends on the formation of nascent orthoformic ether. The secondary product from the formation of the orthoformic ether was proved to be the double chloride of mercury and ammonium by the following analyses:

I. 0.3027 gram substance gave 0.2173 gram HgS.
II. 0.3022 gram substance gave 0.2160 gram HgS.
III. 0.3007 gram substance gave 0.4027 gram AgCl.

	Calculated for NH_4HgCl_3.	Found. I.	II.	III.
Hg	61.66	61.88	61.61	....
Cl	32.84	....	....	33.11

Zincic cyanide gave, when heated in the same way as the mercuric cyanide, a zinc double salt of the chloride of formiminoethyl ether, but, as it is very deliquescent, the mercury salt is to be preferred for practical purposes. Argentic cyanide, or potassic cyanide, yielded no result.

Contributions from the Chemical Laboratory of Harvard College.

THE ACTION OF BROMINE ON 2,6-DIBROMPARAPHENYLENEDIAMINE.

By C. Loring Jackson and D. F. Calhane.

The object of this research was to make a more careful study of the conversion of paraphenylenediamines into quinones, and, as we hoped that the intermediate products might be more stable if the benzol ring was loaded with atoms of

bromine, we first tried to make the tetrabromparaphenylenediamine, a substance prepared some years ago in this laboratory but not as yet described. For this purpose we dissolved some of the 2,6-dibromparaphenylenediamine in absolute ether and treated it with bromine also diluted with ether, but the reaction did not run as we had expected, for instead of a slightly colored substitution-product we obtained a dark but vivid green precipitate, which seems to be one of the products intermediate between the diamine and the quinone, of which we were in search. The analysis of this substance, which looks much like a good specimen of chromic oxide, gave numbers corresponding to the formula $C_6H_2Br_2(NH)_2HBr$, and that it was a bromide was shown by the action of an aqueous solution of sodic carbonate, which set free a base dissolving in ether with a blood-red color, with the formation of the calculated amount of sodic bromide. The red solution of the base was also obtained by shaking the green bromide with ether and ammonia gas, or an amine. Such a solution gave, with hydrobromic acid gas or hydrochloric acid gas, a green precipitate exactly like the original. The chloride contained an amount of chlorine corresponding to $C_6H_2Br_2(NH)_2HCl$.

The percentage composition of the diimine is so near to that of the diamine that it was possible a considerable amount of the bromide of the latter might be mixed with the colored salt, and to settle this point the preparation of the green salt was carried on quantitatively, when it was found that the amount of bromine used corresponded to 1 molecule of bromine to 2 molecules of the 2,6-dibromparaphenylenediamine. It follows therefore that the action is most simply expressed by this reaction,

$$2C_6H_2Br_2(NH_2)_2 + Br_2 = C_6H_2Br_2(NH)_2HBr + C_6H_2Br_2(NH_2)_2HBr,$$

and that about one-half of the green precipitate consists of the bromide of the diamine. That this reaction did not run perfectly smoothly was shown by the fact that the filtrate in these quantitative experiments was colored red probably by some of the free diimine. We have not as yet obtained either

the diimine or its salt free from this impurity of diamine, because our work has been much retarded by the pressure of other duties. Our reason for publishing the paper in this unfinished state is that we cannot continue the work together owing to the departure of one of us from Cambridge.

The arguments in favor of considering the colored base, the diimine, $C_6H_2Br_2(NH)_2$, are, that the formula explains simply the formation of the substance from bromine and the diamine, and also the color and slight stability of the compound. We are aware that these arguments are not convincing, but were prevented for the reason already given from furnishing an experimental proof of its structure. We had, in fact, tried several experiments with reducing agents on the salt, but we prefer not to publish these until further work in this direction has led to definite results. In the absence of these we adopt, provisionally, the theory that our new substance is a diimine.

The free base is so unstable that we did not succeed in purifying it for analysis, or in making the acetyl or benzoyl derivative. It decomposes quickly into a brown substance dissolving in ether with a brown color. This part of the subject will also be studied more carefully in the coming year.

That this colored base is a step in the conversion of diamines into quinones seems evident from the facts that the 2,6-dibromparaphenylenediamine is converted into 2,6-dibromquinone by treating it with bromine and water, and that the colored salt gives the same product with the same reagents.

Paraphenylenediamine, when treated with bromine in anhydrous ether, gives a similar precipitate of a somewhat brighter blue than Prussian blue, which, on analysis, gave results agreeing fairly well with the formula $C_6H_4(NH)_2HBr$. This blue precipitate was undoubtedly contaminated with some of the green $C_6H_2Br_2(NH)_2HBr$, as an excess of bromine converted the blue product into this green salt, but our analytical data are near enough to show that the first action of the bromine consists in the modification of the amino groups and not in the replacement of the hydrogen of the benzoyl ring. This blue salt also undoubtedly contains a large quantity of

the bromide of paraphenylenediamine. It is more stable than the green salt, as it is less decomposed by water or alcohols, which is probably due to the fact that the basic properties of the diimine are not neutralized by the presence of bromine in the ring here, as they are in the green $C_6H_2Br_2(NH)_2HBr$. Orthophenylenediamine gives, under the same conditions, a colored precipitate similar to that from the paradiamine, but much less stable. Metaphenylenediamine, on the other hand, when treated with bromine in anhydrous ether, gives only a white precipitate, undoubtedly a substitution-product.

Hencke[1] obtained a substance which seems to belong to the same class as our so-called diimines, by the action of plumbic dioxide on paraminodiphenylamine, $NH_2C_6H_4NHC_6H_5$, in ethereal solution. The product gave results on analysis corresponding to the formula $C_6H_4NHNC_6H_5$, had a brown color, and gave a bluish-green color with glacial acetic acid. Hencke, however, thinks that it is not a simple diimine, but has a higher molecular weight.

For the sake of comparison in our attempts to make the benzoyldiimine we were obliged to make the monobenzoyl-2,6-dibromparaphenylenediamine,

$$C_6H_2Br_2NH_2NHCOC_6H_5,$$

which melts at 194°.

All the colored substances mentioned above will be submitted to a more careful study during the coming year in this laboratory, and attempts will be made to prepare other substances of the same class.

EXPERIMENTAL PART.

Action of Bromine upon 2,6-Dibromparaphenylenediamine in Absolute Ether.

The 2,6-dibromparaphenylenediamine used in this work was prepared from paranitraniline, which was dissolved in strong hydrochloric acid by the aid of heat, the solution diluted with water to a volume of about 5 liters, and treated with a stream of air saturated with bromine vapor until the liquid showed a permanent red color. The precipitate of dibromni-

[1] Ann. Chem. (Liebig), 255, 193 (1889).

traniline thus obtained was next reduced to the dibromparaphenylenediamine with tin and hydrochloric acid. It was found convenient to use not more than 25 grams in each reduction, and in this case the action was complete after heating in a flask on the steam-bath for four or five hours. Two methods were used in working up the product of the reduction, neither of which, however, gave a satisfactory yield. The simplest method consisted in precipitating the diamine with sodic hydrate, which was not added in sufficient amount to redissolve completely the hydrates of tin, the precipitate was filtered out, dried, powdered, and extracted with a boiling mixture of equal volumes of ligroin and benzol. In the second method the liquid poured off from undissolved tin was allowed to stand in a cool place until the double tin salt had separated. This was filtered out, washed with cold water, dissolved in hot water, and saturated with sulphuretted hydrogen. The filtrate from the sulphide of tin was rendered strongly alkaline with sodic hydrate, this being added in sufficient quantity to redissolve any hydrate of tin present, and then extracted with ether in a continuous extractor.

The anhydrous ether used in these experiments was prepared by shaking common ether two or three times with water, drying it for twenty-four hours over calcic chloride, for twenty-four hours over sodium, and distilling over sodium. Two grams of the 2,6-dibromparaphenylenediamine were dissolved in 100 cc. of this anhydrous ether, and 0.2 cc. of bromine was also dissolved in 100 cc. of the ether. After both solutions had been cooled with ice, they were mixed, when a heavy green precipitate was formed, which was filtered out, washed with anhydrous ether, dried *in vacuo*, and analyzed with the following results:

I. 0.1572 gram substance gave, by the Carius method, 0.2562 gram AgBr.

II. 0.1974 gram substance gave 0.3196 gram AgBr.

III. 0.3594 gram substance gave 24.3 cc. moist N, at 28° and 765 mm. pressure.

IV. 0.2372 gram substance gave 18 cc. moist N, at 17° and 768 mm. pressure.

V. 0.4822 gram substance gave, on combustion, 0.3752 gram CO_2 and 0.1146 gram H_2O.

	Calculated for $C_6H_2Br_3(NH)_2HBr$.	Found. I.	II.	III.	IV.	V.
Br	69.56	69.33	68.89	....	....	....
N	8.12	....	....	7.47	8.90	....
C	20.86	....	....	....	....	21.22
H	1.45	....	....	....	....	2.64

As most of these analyses were made with specimens from different preparations, there is no doubt that the precipitate has a constant composition.

The results of the combustion are not so near to the percentages required by the formula as we could wish, but, as hydrobromic acid is given off rapidly by this easily decomposed substance, we could hardly expect better results. A specially long porcelain boat was used, and the substance was mixed in it with a quantity of a mixture of 8 parts of plumbic chromate and 1 part of potassic dichromate. Plumbic chromate also replaced almost all the cupric oxide in the tube.

The results obtained seemed to indicate that the substance is the bromide of the 2,6-dibromparaphenylenediamine.

Two grams of the diamine gave from 1.8 to 1.95 grams of diimine bromide, whereas the theory requires 2.59 grams. The yield, therefore, was 75 per cent of that demanded by the theory.

Another confirmation of this theory of the nature of our compound was given by its behavior with sodic carbonate, which converted it into a brownish-red substance with the formation of sodic bromide. The amount of bromine removed was determined as follows:

0.5226 gram green salt gave, after decomposition with an aqueous solution of pure sodic carbonate, 0.2830 gram AgBr.

	Calculated for $C_6H_2Br_3(NH)_2HBr$.	Found.
Br	23.19	23.45

It is hardly possible that this reaction can be other than the conversion of a salt into the corresponding free base.

To settle this point more completely the following experiment was tried: One-tenth gram of isoamylamine was dis-

solved in 25 cc. of anhydrous ether, and 0.5 gram of the green salt was added to this solution in small portions at a time, shaking the mixture thoroughly after each addition. The mixture was allowed to stand five minutes and then filtered from isoamylamine bromide into a test-tube containing 30 cc. of dry ether, 5 cc. of which had been saturated with hydrochloric acid gas. The blood-red filtrate, as soon as it came in contact with the hydrochloric acid, formed a deep-green precipitate, which could not be distinguished by the eye from the original bromide. This was washed thoroughly with ether, dried, and the amount of chlorine removed from it by aqueous sodic carbonate determined as follows:

0.1935 gram substance gave 0.0887 gram AgCl.

	Calculated for $C_6H_2Br_2(NH)_2HCl$.	Found.
Cl	11.81	11.31

These results leave no doubt that we have here a red base, which forms a green bromide or chloride, but they do not prove that the substance is pure, as the analyses cannot determine between the salt of a diimine and a diamine, and in fact the work next to be described showed that the green precipitate was a mixture containing a considerable quantity of the bromide of the diamine mixed with the colored salt. The object of these experiments was to trace quantitatively the formation of the green bromide. This was done by the use of a standard solution of bromine in anhydrous ether, which was added to the ethereal solution of the 2,6-dibromparaphenylenediamine until a drop acted on a potassic iodide and starch paste paper.

At first we tried the action of undiluted bromine on the ethereal solution of the diamine, but found that the reaction was too violent. A solution of bromine in chloroform also gave bad results, as shown by the dirty color of the precipitate. We were obliged, therefore, to use a solution of bromine in anhydrous ether, and succeeded in getting good results, if the solutions were used as soon as they were made, since they deteriorate rapidly from the substituting action of the bromine on the ether.

I. A solution of bromine in anhydrous ether, containing 0.006 gram of bromine in each cubic centimeter, was used. Five-tenths gram of the 2,6-dibromparaphenylenediamine were dissolved in anhydrous ether, and to this was added a mixture of 25 cc. of the solution of bromine diluted with its own volume of ether. The titration was then finished by adding the solution of bromine from a burette; 26 cc. of the solution of bromine were needed.

II. The solution used contained 0.015 gram in the cubic centimeter. Five-tenths gram of the 2,6-dibromparaphenylenediamine dissolved in anhydrous ether required 10 cc. of this solution.

	Calculated for $C_6H_2Br_2(NH_2)_2$.	Calculated for $2C_6H_2Br_2(NH_2)_2$.	Found. I.	Found. II.
Br	0.3007	0.1504	0.1560	0.1500

Under the heading "calculated" the amount of bromine in grams is given, which would be used if 1 molecule of bromine acted on 1 or 2 molecules of the diamine. The results show that each molecule of bromine acted on two of the 2,6-dibromparaphenylenediamine instead of on one, as would be the case if the green precipitate were the pure salt of the diimine. If, then, the diimine is really formed, the reaction runs as follows:

$$2C_6H_2Br_2(NH_2)_2 + Br_2 = C_6H_2Br_2(NH)_2HBr + C_6H_2Br_2(NH_2)_2HBr,$$

and the product is a mixture of the bromides of the diamine and diimine. This view is supported by the fact that the ethereal filtrate from the green precipitate contained no hydrobromic acid. It had, however, a strong red color, which indicated that it contained some of the diimine and that the reaction did not run with perfect smoothness.

In the preceding discussion we have called our colored product the diimine, but the data at our disposal are not sufficient to establish its nature with certainty, and we feel it will be wiser to postpone all description of the reduction-experiments undertaken for this purpose until they have led to some definite result.

Properties of the Bromide of 2,6-Dibromparaphenylenediimine(?).—The specimens prepared by us all contained a considerable proportion of the bromide of the diamine, but the properties given here are such that the presence of this impurity would not interfere with them. It forms a dark but vivid green powder, looking like a fine specimen of chromic oxide. Water changes its color from green to purplish-black. Alcohol turns it red, probably from the formation of the free base. This decomposition is more rapid when the alcohol is hot, much less rapid when absolute alcohol is used instead of common alcohol. Chloroform seems to have no action on it in the cold, but decomposes it slowly when boiling. Isoamyl alcohol is colored red by it, showing apparently the formation of the free base. Strong hydrochloric acid dissolves it with a deep purplish color, and the diluted solution deposits, on standing, a dark purple, flocculent precipitate. Sodic carbonate in aqueous solution decomposes it, forming a brown precipitate of the free base. This reaction was used in the analysis of the substance. The free base thus formed dissolves, if fresh, in ether, benzol, or acetone with a blood-red color. The red solution is most conveniently obtained by treating the bromide suspended in anhydrous ether with gaseous ammonia or an amine. That it was the base was shown by treating its ethereal solution with gaseous hydrobromic acid or hydrochloric acid, when a green precipitate of the bromide or chloride was formed. The chloride could not be distinguished by the eye from the bromide. The free base was very unstable, passing in a very short time into a substance which gave a brown solution in ether. All our attempts to obtain the free base in a pure state for analysis, or to make its benzoyl, or acetyl derivative failed, but these experiments will be resumed in the coming year in this laboratory, and its brown decomposition-product will also be studied.

Action of Bromine on Paraphenylenediamine in Ethereal Solution.

Six-tenths of a gram of paraphenylenediamine were dissolved in 250 cc. of anhydrous ether and cooled thoroughly

with ice. To this solution was added a mixture of 0.15 cc. of bromine and 75 cc. of anhydrous ether, also cooled with ice, when a brilliant blue precipitate was obtained, which yielded the following results on analysis:

I. 0.2464 gram substance gave, by treatment with sodic carbonate in aqueous solution, 0.2410 gram AgBr.

II. 0.2348 gram substance gave 0.2292 gram AgBr.

	Calculated for $C_6H_4(NH)_2HBr$.	Found. I.	II.
Br	42.79	41.63	41.55

0.3105 gram substance gave, by the Carius method, 0.3401 gram AgBr.

	Calculated for $C_6H_4(NH)_2HBr$.	Found.
Br	42.79	46.60

These results leave much to be desired, but are explained by the fact that an excess of bromine acts upon the blue substance converting it into the green 2,6-dibromparaphenylenediimine bromide just described, as we proved by a special experiment. It was hardly to be expected, therefore, that we should get the blue precipitate entirely free from the green one containing more bromine. Our analyses, although so imperfect, are given, because they show that the action of the bromine is exerted on the amino groups before it begins to replace the hydrogen of the ring.

Properties of the Bromide of Paraphenylenediimine(?).—The preparation undoubtedly contained a large proportion of the bromide of the diamine. It forms a dark blue powder looking like Prussian blue, but rather lighter in color. It is more stable than the green dibrom compound, and it is sparingly soluble in water, apparently without decomposition. It is also more stable toward alcohol, in which it dissolves with the formation of only a slight red color. Chloroform does not decompose it apparently, even when hot. Cold isoamyl alcohol dissolves it without change of color, but, when the solution is boiled, it turns red.

Orthophenylenediamine, when treated with bromine in anhydrous ether, also gave a colored precipitate, which was far

less stable than that formed from the paradiamine. Metaphenylenediamine, under these conditions, gave a white precipitate, obviously a substitution-product.

Monobenzoyl-2,6-dibromparaphenylenediamine, $C_6H_2Br_2NH_2NHCOC_6H_5$.—This substance was made in order to compare it with the products obtained by the action of benzoyl chloride on our red base. As we cannot find that it has been described, we give an account of it.

Two grams of 2,6-dibromparaphenylenediamine were dissolved in 100 cc. of ether, and the calculated amount of benzoyl chloride, diluted with ether, added. The copious white precipitate thus formed was filtered off, washed with water, dried, and recrystallized from dilute alcohol until it showed the constant melting-point 194°, when it was dried *in vacuo* and analyzed with the following result:

0.2303 gram substance gave, by the Carius method, 0.2338 gram AgBr.

	Calculated for $C_6H_2Br_2NH_2NHCOC_6H_5$.	Found.
Br	43.24	43.20

Properties of the Monobenzoyl-2,6-dibromparaphenylenediamine.—It crystallizes in short, creamy-white prisms with a vitreous luster. It melts at 194°, and is soluble in ethyl or methyl alcohol, glacial acetic acid, or acetone; sparingly soluble in benzol, chloroform, or ligroin; essentially insoluble in ether. The best solvent for it is dilute alcohol. Strong hydrochloric acid has no apparent action on it, even when hot. Fuming nitric acid dissolves it with a yellow color; dilution throws down a white precipitate. Strong sulphuric acid dissolves it in the cold.

Action of Bromine and Water on the 2,6-Dibromparaphenylenediamine.

A specimen of the 2,6-dibromparaphenylenediamine was suspended in cold, dilute hydrochloric acid and treated with bromine in the proportion of 2 molecules of bromine to each molecule of the diamine. The yellow product formed was purified by crystallization from ligroin, when it gave broad,

yellow plates, melting at 126°. As it seemed evident from this that the substance was the dibromquinone melting at 131°, the purification was not continued. The same product seemed to be formed when the green 2,6-dibromparaphenylenediimine bromide was treated with bromine and water.

CAMBRIDGE, MASS., October, 1903.

THE SPECIFIC GRAVITIES OF CADMIUM CHLORIDE AND CADMIUM BROMIDE.

BY GREGORY PAUL BAXTER AND MURRAY ARNOLD HINES.

Recent investigation in this laboratory upon atomic volume[1] has made it desirable to obtain the densities of certain salts with great accuracy. If a solid is of such a nature that it may be easily obtained in a pure state, the determination of its specific gravity offers no especial difficulties. The "inclusion" of mother-liquor which takes place whenever salts are formed from solution,[2] and the danger of incomplete expulsion of all crystal and "adsorbed" water make the determination of the specific gravity of a salt a more or less uncertain process, unless precautions are taken to avoid these pitfalls. In the case of the halogen salts of cadmium, the tendency to become basic when they are heated in a moist condition is an additional source of error. Thus it is not surprising that the values heretofore obtained for the specific gravity of cadmium chloride vary between 3.65 and 3.94,[3] and those for cadmium bromide between 4.71 and 4.91.[4]

In this investigation the method employed for preparing very pure, dry cadmium chloride was that of igniting a double chloride of cadmium and ammonium in a current of hydrochloric acid gas. A salt of the formula $CdCl_2NH_4Cl$ has been described,[5] which for this purpose has the great advantages of containing no water of crystallization, and a small proportion of ammonium chloride.

[1] Richards: Proc. Am. Acad., 37, 3, 399; 38, 293.

[2] Richards: Proc. Am. Phil. Soc., 42, 28 (1903).

[3] Bödeker: Die Beziehung zwischen Dichte und Zusammenhang bei festen und liquiden Stoffen (1860), 3.625; Clarke: Am. J. Sci., [3], 16, 202 (1878), 3.938 at 23°; Clarke: This JOURNAL, 5, 240 (1883), 3.655 at 17°.

[4] Clarke: This JOURNAL, 5, 240 (1883), 4.794 at 20°; Bödeker: *Loc. cit.*, 4.712–4.91.

[5] Rimbach: Ber. d. chem. Ges., 30, 3073 (1897).

A quantity of the double salt was prepared by dissolving cadmium and ammonium chlorides in the above proportions and evaporating the solution to the point of crystallization. The crystals were separated from the mother-liquor, recrystallized several times from pure water, dried between filter-papers, and exposed to the air for a short time. In order to make certain that the crystals possessed the desired composition, analysis of the air-dried salt was carried out as follows: A weighed sample of the double chloride was dissolved in water and the chlorine determined in the usual way by precipitation with silver nitrate. The ammonia was estimated by decomposing the salt with sodium hydroxide and distilling into standard acid. Finally, to determine the cadmium, a known amount of the salt was dissolved in an excess of potassium cyanide and the solution was electrolyzed in a weighed platinum crucible.

	Calculated for $CdCl_2NH_4Cl$.	Found.
Cl	44.97	44.88
		44.82
NH_4	7.60	7.60
		7.67
Cd	47.42	47.26
		47.48

The composition of our salt is evidently that already cited.

In order to show that ignition of the double salt would give pure cadmium chloride, portions of the salt, contained in a platinum boat, were heated in a tube of hard glass in a current of hydrochloric acid gas, until all sublimation of ammonium chloride ceased. This acid was generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid, and was dried by means of several columns containing beads moistened with concentrated sulphuric acid, and finally by a tube of phosphoric anhydride which had been sublimed in a rapid current of dry air to get rid of phosphorous impurities. Heating for an hour, at first gently, then with the full heat of two Bunsen burners, in a rapid current of gas, was sufficient to remove the last traces of ammonium chloride. After the hard glass tube had been allowed to cool, the hydrochloric acid gas

was displaced by pure dry nitrogen[1] and this in turn by dry air. Finally the boat was transferred to a weighing-bottle without an instant's exposure to moisture by the method so frequently used for the purpose in this laboratory.[2]

The apparatus used for the above operations was constructed entirely of glass, except for a few rubber connections in the apparatus for purifying nitrogen and air.[3] Since these latter gases were subsequently conducted over beads moistened with silver nitrate solution, no sulphur compounds could have been introduced from this source. Cadmium chloride prepared in this way gives a clear solution in water, showing that no basic salt is formed in the process. It was easily proved that all ammonium chloride had been expelled by testing the solution with Nessler's reagent, for no appreciable coloration was produced.

The determination of the specific gravity of cadmium chloride was effected with the aid of a pycnometer constructed especially for the purpose. It is a modification of a pycnometer devised by T. W. Richards for the determination of the specific gravity of solids.[4] The weighing-bottle was provided with two glass stoppers, one of which was of ordinary shape and was used during the weighing of the chloride. Into the other were sealed two capillary tubes which served to fill the vessel with liquid. The weighing-bottle and the pycnometer stopper were both made of thick glass in order to avoid distortion when the stopper was inserted.

As the bottle was more conveniently made with a round

[1] Made by passing air through strong ammonia, then over hot copper gauze, and finally removing the excess of ammonia with sulphuric acid.

[2] Richards and Parker: Proc. Am. Acad., 32, 59.

[3] The apparatus for generating and purifying gases was essentially identical with that used by Richards and Parker in preparing pure magnesium chloride. See Proc. Am. Acad., 32, 67.

[4] A description of this pycnometer will soon be published.

bottom, a platinum carriage was constructed to hold the bottle on the balance pan. This carriage was used in all weighings of the bottle.

Experiments were first undertaken to determine the accuracy with which the pycnometer could be weighed when filled with a liquid. The pycnometer was immersed as far as possible in water at 25°, and was filled exactly to a mark etched upon one capillary. It was then wiped with a slightly dampened cloth and weighed at intervals of five minutes. It was found that a regular loss in weight of nearly 0.3 milligram per minute took place. Although the stopper was reground with emery dust so that it fitted perfectly, it was found impossible to reduce the loss below 0.2 milligram per minute. This difficulty was caused by leakage of water through the glass joint, owing to capillarity and to its subsequent evaporation. In order to prevent this evaporation, 2 or 3 milligrams of soft paraffin were placed on the upper portion of the ground surface of the stopper before it was inserted in the bottle. The pycnometer, when filled with water as before, then remained absolutely constant in weight.

As cadmium chloride was found to be insoluble in toluol, this liquid was used in the determination of the specific gravity of the salt. Toluol was dried over fused caustic potash and then distilled, the first and last portions being discarded. Its specific gravity at 25° was determined, first with the ordinary form of Ostwald pycnometer, then by the pycnometer which has been described. When the pycnometer was filled with toluol the stopper was made tight with syrupy phosphoric acid. For details concerning the filling of the pycnometer, see page 226.

Ostwald Pycnometer.

Weight of pycnometer.	Weight of pycnometer filled with water.	Weight of pycnometer filled with toluol.	Weight of water.	Weight of toluol.	Density of toluol. 25°/4°.
Grams.	Grams.	Grams.	Grams.	Grams.	
6.9548	15.2431	14.1138	8.2883	7.1590	0.86139

New Pycnometer.

Weight of pycnometer and grease.	Weight of pycnometer filled with water.	Weight of pycnometer and phosphoric acid.	Weight of pycnometer filled with toluol.	Weight of water.	Weight of toluol.	Density of toluol. 25°/4°.
Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	
15.5747	25.0540	15.5749	23.7627	9.4793	8.1878	0.86138

An average of the two values, 0.86138, was used in the calculation of the specific gravities of the salts. The agreement of the results obtained by the two pycnometers shows that the new form of pycnometer is capable of giving accurate results. Nevertheless, a confirmatory test was carried out with some very pure fused silver bromide which resulted from a determination of the atomic weight of iron by one of us.[1] The bromide was fused in a porcelain crucible, cooled, and cut into pieces. Two determinations of the specific gravity of the salt were made by displacing toluol in the new pycnometer and two with the Richards pycnometer. In the calculations a vacuum correction of +0.000046 was applied to every apparent gram of silver bromide. No vacuum correction was necessary for the toluol, since the air displaced by the pycnometer filled with toluol was always the same.

Number of determination.	Form of pycnometer.	Weight of AgBr in vacuum. Grams.	Weight of toluol displaced in vacuum. Grams.	Density of AgBr. 25°/4°.
1	New	7.2427	0.9628	6.480
2	"	7.4305	0.9877	6.480
			Average,	6.480
3	Richards	7.0379	0.9361	6.476
4	"	5.0077	0.6660	6.477
			Average,	6.477
		Average of all four determinations,		6.478[2]

[1] Baxter: Proc. Am. Acad., **39**, 245 (1903).

[2] Previous determinations of the density of silver bromide are as follows:
Karsten: J. für Chem. und Physik, **65**, 394 (1931). Precipitated 6.353.
Schröder: Pogg. Ann., **106**, 226 (1859). Precipitated 6.387 to 6.521. Fused 6.315 to 6.428.
Clarke: Am. J. Sci., [3], **13**, 294 (1877). Precipitated 6.215 at 17°.
Rodwell: Phil. Trans., 1882, 1125. 6.245 at 0°.

Less than one-twentieth per cent difference exists between the results obtained by the two pycnometers. This difference corresponds to an error in weighing the displaced toluol of only about 0.5 milligram. Evidently our new pycnometer is suitable for the purpose.

Purification of Materials.

Ammonium Chloride.—One kilogram of ammonium chloride was dissolved in water, 100 cc. of concentrated nitric acid were added, and the solution was boiled for several days to destroy the amines. The salt was then crystallized six times from pure water. Ammonia was generated from this ammonium chloride by means of sodium hydroxide and was absorbed in pure water. Ammonia was again evolved by heating the solution of ammonium hydroxide and was collected in pure redistilled hydrochloric acid in a platinum dish. The resulting ammonium chloride was crystallized once from pure water.

Cadmium.—Five hundred grams of cadmium sulphate were dissolved in about 2.5 liters of water, and 300 cc. of concentrated hydrochloric acid were added to the solution. Hydrogen sulphide was then passed into the solution to saturation. After the cadmium sulphide thus formed had been thoroughly washed by decantation, it was dissolved in redistilled nitric acid and the cadmium nitrate was crystallized several times from pure water, the last two crystallizations being carried out in platinum vessels. The nitrate was dissolved in water, enough pure redistilled sulphuric acid to convert the nitrate into the sulphate was added, and the solution was heated on a steam-bath until all the nitric acid was expelled. An aqueous solution of the sulphate was then electrolyzed, a platinum dish which contained the solution acting as cathode. The deposit consisted of fine crystals, but adhered strongly to the dish and could be washed without difficulty. Finally the cadmium was dissolved in pure hydrochloric acid, which had been distilled with a platinum condenser into a platinum dish.

In order to prepare the double chloride, the purified ammonium chloride was added to the solution of cadmium chloride in slight excess of the amount required by the formula

$CdCl_2NH_4Cl$. The solution was allowed to stand over pure metallic cadmium for one week and was then evaporated to crystallization. Finally the double salt was recrystallized several times from the purest water in a platinum dish, and the crystals were dried as completely as possible in a vacuum desiccator containing fused potassium hydroxide.

The method of procedure was as follows: The weight of the pycnometer, containing the empty platinum boat and filled with toluol at 25°, was determined twice. From these weights and the weight of the pycnometer and boat alone, the weight of toluol contained by the pycnometer was obtained. In each experiment, after the bottle had been weighed with the salt, the ordinary stopper was removed and sufficient toluol was introduced completely to cover the boat and salt. Then the system was placed in a desiccator which was immediately exhausted by means of a powerful air-pump. Next the pycnometer stopper, which had been weighed with the small amount of syrupy phosphoric acid necessary to make the ground joint tight, was inserted and the pycnometer was filled with toluol exactly to the mark, in a constant temperature-bath. In order to avoid any error from absorption of water by the phosphoric acid, the stopper was inserted immediately after weighing. Finally, the pycnometer was wiped with a slightly dampened cloth and weighed after a few moments' standing in the balance case. From the weight of the system thus obtained, the weight of the salt, and the weight of toluol contained by the pycnometer with the empty boat, was calculated the weight of toluol displaced. The cleansing of the boat in Experiments 4 and 5 caused a loss in weight of a few tenths of a milligram, so that theoretically the toluol content of the pycnometer increased. The weight of toluol displaced by this small quantity of platinum is, however, too minute to be taken into consideration. In the calculations a vacuum correction of +0.00015 gram was applied to every apparent gram of cadmium chloride. Needless to say, the gold-plated brass weights were carefully standardized to tenths of a milligram, and the corrections for the thermometer at 0° and 32°.38 were determined.

Number of determination.	Weight of $CdCl_2$ in vacuum.	Weight of toluol displaced in vacuum.	Density of $CdCl_2$. 25°/4°.
	Grams.	Gram.	
5	2.8842	0.6136	4.049
6	2.1876	0.4660	4.044
7	3.0639	0.6517	4.050
8	0.9821	0.2087	4.054
9	3.1245	0.6647	4.049
		Average,	4.049

In the cooled salt, which was transparent and crystalline, were visible a very few minute bubbles of gas; hence the observed specific gravity is slightly too low. Furthermore, a trace of platinum was visible in some cases. Whether this platinum had its source in the attacking of the boat, or was contained in the original salt, was uncertain. The boat did not perceptibly lose in weight, however, except in the cases when it was subjected to scrubbing with sand during the cleansing. At all events the amount of this platinum was too small to have had an appreciable effect upon the specific gravity.

The specific gravity of cadmium bromide was determined with a sample of salt prepared by O. W. Huntington for use in the determination of the atomic weight of cadmium.[1] The salt was fused in a platinum boat in a current of pure nitrogen and hydrobromic acid gases, and bottled in dry air as previously described. The apparatus for generating hydrobromic acid was that employed by one of us in a determination of the atomic weight of iron,[2] and the purest bromine was used for the purpose. After the salt had been weighed, its specific gravity was determined by displacement of toluol in the pycnometer used in the work upon the chloride.

Number of determination.	Weight of $CdBr_2$ in vacuum.	Weight of toluol displaced in vacuum.	Density of $CdBr_2$. 25°/4°.
	Grams.	Grams.	
10	6.1535	1.0201	5.196
11	6.6920	1.1095	5.196

In both of these analyses the boat was somewhat attacked and a small amount of metallic platinum was found suspended

[1] Proc. Am. Acad., 17, 29 (1882).
[2] *Ibid.*, 39, 250 (1903).

in the fused salt. But since the platinum was not removed from the boat during the determination of the specific gravity of the salt, no error could have resulted from this cause. A vacuum correction of +0.00009 was applied to every apparent gram of the cadmium bromide.

A discussion of the earlier determinations of the specific gravities of the salts under consideration is impossible, since no descriptions of the experiments are given. In no case is there evidence of any attempt at purification. Slight variations in specific gravity are to be expected as the result of differences in treatment of a salt, but the great disagreement of our results with previous values cannot be explained in this way. Moreover, Bödeker's work on densities has already been shown to be inaccurate in many cases.[1] The great pains which was taken in the purification of our salts and in the carrying out of the determinations leads us to the conclusion that our results represent very nearly the truth. Certainly it is almost inconceivable that they should be too high. Our cadmium chloride, in especial, showed the outward appearance of sufficient purity for even an atomic weight determination. Such an investigation is now in progress.

To sum up the results of this research :

1. Pure anhydrous cadmium chloride was prepared.

2. A pycnometer was devised for the determination of the density of very hygroscopic substances.

3. The specific gravities of the following fused salts at 25° referred to water at 4° were determined :

Silver bromide	6.478
Cadmium chloride	4.049
Cadmium bromide	5.196

We are indebted to Dr. Wolcott Gibbs and to the Cyrus M. Warren Fund for Research for many indispensable platinum vessels.

HARVARD UNIVERSITY,
CAMBRIDGE, MASS.

[1] Richards : Proc. Am. Acad., 31, 163. See also following paper in this JOURNAL.

THE SPECIFIC GRAVITY OF ZINC CHLORIDE.

By Gregory Paul Baxter and Arthur Becket Lamb.

Two chief obstacles arise in the determination of the specific gravity of zinc chloride, the extremely hygroscopic character of the substance, and the great tendency which it shows to form a basic salt when heated in a moist condition. Lorentz[1] and Czepinski[2] have found that only by electrolysis of the fused salt could the last traces of water be eliminated. Since the removal of water by electrolysis seemed impracticable for the purpose in hand, recourse was had to the method of heating the double chloride of zinc and ammonium, $ZnCl_3NH_4Cl$,[3] in a current of dry hydrochloric acid gas until all of the ammonium chloride had been expelled. The double salt crystallizes without water of crystallization, and is not hygroscopic, hence it seemed reasonable to suppose that an anhydrous product could be thus obtained. A similar method has been used already by Richards and Parker[4] in preparing dry magnesium chloride, and by Baxter and Hines[5] in the preparation of dry cadmium chloride.

In order to settle this point, a quantity of the double salt was prepared by dissolving the proper amounts of ammonium and zinc chlorides in water, then evaporating the solution nearly to saturation and allowing the solution to cool. The resulting zinc ammonium chloride was highly crystalline, and stable in the air. In order to remove as far as possible the adhering and included water, it was exposed for several days in a finely powdered condition in a desiccator over sulphuric acid and finally over phosphorus pentoxide. Samples of the salt, contained in a porcelain boat, were heated in a hard glass tube in a current of dry hydrochloric acid gas for from one to two hours, at first gently, but finally with the full heat of two Bunsen burners. The residual fused salt, when dissolved in pure water, gave a clear solution, hence it must have been free from oxychloride. Furthermore, this solution

[1] Ztschr. anorg. Chem., **10**, 85.
[2] *Ibid.*, **19**, 228.
[3] Ztschr. anorg. Chem., **37**, 199 (1903).
[4] Proc. Am. Acad., **32**, 59.
[5] See preceding paper in this Journal.

gave no test for ammonia with Nessler's reagent. Zinc ammonium chloride is, then, a suitable source of anhydrous zinc chloride; therefore a quantity of the pure double salt was prepared.

Purification of Materials.

Nine hundred cc. of pure concentrated hydrochloric acid were diluted with twice this volume of water and shaken with a few crystals of potassium permanganate, to set free any bromine or iodine which might have been present. It was then distilled through a platinum condenser and the middle fraction of about 600 cc. was collected in a platinum vessel. In order to prepare ammonia free from amines, ammonium chloride was boiled with concentrated nitric acid and a solution of the recrystallized salt was heated with an excess of sodium hydroxide. A solution of this ammonia was distilled into some of the above hydrochloric acid in a platinum dish, and the resulting ammonium chloride was recrystallized several times from the purest water.

Two hundred and fifty grams of zinc were treated with about 3 liters of 10 per cent sulphuric acid and the containing flask was allowed to stand upon a steam-bath for a week, until nearly all of the zinc had dissolved. Since on cooling the solution some basic salt was precipitated, a few drops of concentrated sulphuric acid were added to dissolve the basic salt, and then hydrogen sulphide was passed into the solution until considerable precipitate had been formed. The precipitate, which consisted chiefly of zinc sulphide, was white from the very first, showing that only traces of metals of the copper group could have been present. The filtered solution was heated for some time with about 10 cc. of concentrated nitric acid, in order to oxidize completely any ferrous salt, and a quantity of very pure sodium hydroxide, sufficient to produce permanent precipitation, was added. After several days' standing, the precipitate of zinc carbonate and ferric hydroxide was removed by filtration and a few cubic centimeters of strong sodium hydroxide solution were added. This solution had been electrolyzed in order to free it from heavy metals until,

when the platinum cathode was treated with hydrochloric acid, no trace of iron could be detected in this acid. As the precipitate produced by the hydroxide gave a test for iron with potassium thiocyanate, treatment with small amounts of sodium hydroxide was repeated three times until iron could be no longer detected in the precipitate, and then was repeated once again. The zinc sulphate in solution was recrystallized four times from a dilute solution of pure sulphuric acid, which had been added to decrease the solubility of the sulphate. A large quantity of sulphuric acid could not be used, since it prevented the formation of the heptahydrate, by diminishing the aqueous tension of the solution. In order to convert the sulphate into the chloride, metallic zinc was next obtained by electrolysis. The zinc sulphate crystals were dissolved in a minimum amount of water, and ammonia was distilled into the solution until it became clear. The solution was then electrolyzed in a shallow glass dish between platinum electrodes, with a current as large as the heating of the solution would permit. The tree of zinc crystals was frequently removed[1] and the crystals were washed with dilute ammonia and water.[2] In the subsequent processes only platinum vessels were used in the purification. About 25 grams of the pure zinc were dissolved in hydrochloric acid which had been purified as already described. Solution took place stormily, because, no doubt, of a small amount of platinum which the zinc contained, the greater part of which remained undissolved. Mylius and Fromm[3] observed the same phenomenon whenever they had electrolyzed zinc solutions between platinum electrodes. Ammonia, purified as already described, was then passed into the solution of zinc chloride until a slight precipitate had been produced, and a small portion of this solution was saturated with pure ammonia and again electrolyzed. The resulting crystals were placed in the main solution and the whole allowed to stand for a month. During this

[1] Reynolds and Ramsay: J. Chem. Soc., Trans., **31**, 854.

[2] The method employed for the purification of the zinc was essentially that used by Richards and Rogers in their investigation upon the atomic weight of zinc. See Proc. Am. Acad., **31**, 160.

[3] Ztschr. anorg. Chem., **9**, 161 (1895).

time any platinum in solution must have been precipitated. To the solution, after filtration, the amount of pure ammonium chloride necessary to form the double salt was added, the solution was then evaporated to saturation, and the crystals of double salt which separated on cooling were twice recrystallized from the purest water. The mother-liquors were evaporated to dryness and used in the preliminary experiments. Finally the purified salt was dried by prolonged standing over sodium hydroxide in a desiccator, with frequent pulverization.

Method of Experimentation.

The determination of the specific gravity of zinc chloride was carried out in the same manner and with the same apparatus as in the work upon cadmium chloride and bromide by Baxter and Hines.[1] The zinc ammonium chloride, contained in a platinum boat, was first heated in a current of dry hydrochloric acid gas to remove the ammonium chloride. But the boiling-point of this salt lies so near the temperature necessary to drive off the ammonium chloride that in the preliminary experiments either all the ammonium chloride was not removed or else such a small quantity of zinc chloride remained that it was impossible to make an accurate determination of specific gravity. These difficulties were finally avoided by heating gently at first, and almost wholly on top, then raising the temperature as rapidly as the boiling would permit, until no more ammonium chloride was deposited in the cooler parts of the tube. The full heat of two Bunsen burners, one above and one below, was finally applied for about ten minutes. The entire fusion required about an hour and a half. After the tube had been allowed to cool, the hydrochloric acid was displaced by dry nitrogen, and this, in turn, by dry air. The boat was next transferred to a weighing-bottle, without exposure to moist air, by means of the bottling apparatus usually employed for the purpose in this laboratory. The weight of the zinc chloride was then determined.

The pycnometer employed consisted of the weighing-bottle

[1] See preceding paper.

used in the weighing of the salt, into which a pycnometer stopper had been carefully ground. After the weighing of the salt the ordinary stopper was removed and sufficient dry toluol was introduced to cover the salt. The weighing-bottle was then placed in a vacuum-desiccator which was exhausted by means of an air-pump. Finally the pycnometer stopper was inserted and the pycnometer was filled with toluol exactly to a mark on the stem, while the system was immersed in a constant temperature-bath at 25°. The room in which the adjustment was carried out was kept at a temperature within a few tenths of a degree of 25° during the experiment. The thermostat itself was divided into two compartments, so arranged that the pycnometer, immersed as far as possible in water in the inner compartment, was below the level of the water in the outer compartment. After being filled, the pycnometer was wiped with a damp cloth and allowed to stand in the balance case a short time before it was weighed.

After an experiment was completed, the salt, which was translucent, was dissolved in water, a clear solution being always obtained. The aqueous solution was then tested with Nessler's reagent for ammonia, invariably with negative results. A trace of platinum was visible in the fused salt, but was too small in amount to be determined. This platinum may have had its source in the attacking of the boat, although this did not lose in weight perceptibly, or it may have been due to incomplete removal of the platinum introduced during the electrolysis of the zinc. In one case the toluol from the pycnometer was treated with a solution of ammonium sulphide, without the formation of a trace of precipitate, showing that zinc chloride is insoluble in toluol.

The toluol was freed from methylthiophene by repeated shaking with concentrated sulphuric acid, then washed with water, and, after standing over fused sodium hydroxide for some time, was distilled. The end fractions were discarded, although the boiling-point did not perceptibly change during the distillation. The following successive determinations of its specific gravity were carried out with an Ostwald pycnometer:

	Weight of pycnometer. Grams.	Weight of pycnometer filled with water. Grams.	Weight of pycnometer filled with toluol. Grams.
1	7.6536	16.0094	14.8707
2	7.6533	16.0094	14.8707
3	7.6534	16.0095	14.8707
4	7.6533	16.0094	14.8707
5	7.6534	.....	.....
Averages,	7.6534	16.0094	14.8707

From these data the density of our toluol at 25° referred to water at 4° is found to be 0.86138, a value which is identical with that of the sample prepared by Baxter and Hines.

In the following table are given the results of five consecutive determinations of the specific gravity of fused zinc chloride. A vacuum correction of +0.00027 was applied to every apparent gram of salt. Since the air displaced by the system filled with toluol with and without the salt was the same, no vacuum correction for the toluol was necessary :

Number of experiment.	Weight of zinc chloride in vacuum. Gram.	Weight of displaced toluol in vacuum. Gram.	Density of zinc chloride. $25°/4°$.
1	0.3036	0.0901	2.902
2	0.5982	0.1792	2.875
3	0.9671	0.2860	2.913
4	0.3232	0.0946	2.943
5	0.9243	0.2742	2.904
		Average,	2.907

The average of Experiments 3 and 5, in which the largest quantities of material were used, is 2.908. If each experiment is weighted according to the quantity of salt employed, the mean value becomes 2.905. Such slight differences are beyond the limit of accuracy of the work, since the maximum amount of toluol displaced was never as much as 0.3 gram. There can be no doubt that the specific gravity of fused zinc chloride is slightly less than 2.91.

The only other determination of the specific gravity of zinc chloride of which we have been able to find mention, was made by Bödeker in 1860,[1] who obtained the value 2.753. In

[1] Die Beziehung zwischen Dichte und Zusammenhang bei festen und liquiden Stoffen.

the light of the difficulty in preparing the salt in a pure condition, it is easy to see why his result is lower than ours, for the presence of water would have had the effect of lowering the observed density.

Needless to say, the weights were carefully standardized to tenths of a milligram, and the corrections for the thermometer at 0° and 32°.38 were determined. Reagents were purified whenever this seemed necessary. Water was distilled twice, once over alkaline potassium permanganate and once over dilute sulphuric acid with a block-tin condenser. In short, every precaution was taken that would be necessary in the most accurate analytical work. The appearance and behavior of the zinc chloride was such as to warrant the assumption of sufficient purity for an atomic weight investigation. Such an investigation is planned for the near future.

We are indebted to Dr. Wolcott Gibbs and to the Cyrus M. Warren Fund for Research for many indispensable platinum vessels.

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Contributions from the Chemical Laboratory of Harvard College.

THE NEPHELOMETER, AN INSTRUMENT FOR DETECTING AND ESTIMATING OPALESCENT PRECIPITATES.

BY THEODORE WILLIAM RICHARDS AND ROGER CLARK WELLS.

The gravimetric determination of the finely divided scanty precipitate commonly called an opalescence is a very difficult matter, yet this type of quantitative estimation is often required in analytical work, and is very necessary in many investigations of atomic weights. The apparatus here described is designed to determine these precipitates in quantities under 1 or 2 milligrams per liter of suspending solution. Most of the experiments were made with silver chloride, but the apparatus and method are widely applicable. The method depends upon the facts that these precipitates reflect light, and that the intensity of the light reflected is a function of

the quantity of precipitate, when other conditions are constant.

Before giving a description of the present apparatus it might be well to mention the forms used by previous investigators. Gay-Lussac, the inventor of the volumetric method of estimating silver, does not seem to have used any special apparatus for judging the amount of opalescence. Mulder,[1] however, kept his flasks, containing silver chloride, in metallic boxes blackened upon the inside, and usually observed the production of an opalescence in a solution by raising the flask into the diffused light of a room near a window. Sometimes he decanted the mother-liquor into small vials in which he produced and compared opalescent precipitates. His comparison, however, was wholly a matter of judgment; no measuring device entered into it.

Stas[2] constructed an instrument for estimating the amount of suspended precipitate. Four tubes with perfectly plain bottoms, about 4 cc. in diameter, were supported, adjacent to each other, upon a shelf over holes of the same diameter as the tubes. Beneath the shelf was placed an illuminated scale, and everything above the shelf was in darkness. When the marks on the scale, viewed through two heights of opalescent solution, appeared equally illuminated, Stas assumed that there was an equal weight of precipitate in the two volumes. The great disadvantage of this instrument is that the light is transmitted through the precipitate. If, instead, the reflected light is observed, when a powerful beam is allowed to fall upon the precipitate obliquely, the delicacy of the estimation is greatly increased.

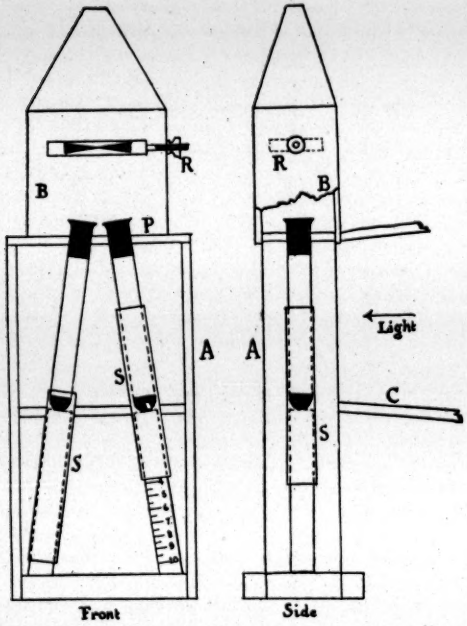
Depending upon the latter fact, the instrument which one of us devised several years ago and named the "nephelometer" was better adapted to compare opalescent precipitates. As it has already been described in a paper upon the atomic weight of strontium,[3] it will suffice to mention the essential characteristics. Two test-tubes were arranged almost vertically, but slightly inclined toward one another so that the eye could

[1] Mulder: Die Silber Probiermethode, p. 23, Trans., Grimm, Leipzig, 1859.
[2] Stas: Œuvres, 1, 155 (1894).
[3] Richards: Proc. Am. Acad., 30, 385 (1894).

look into both. Around the test-tube were two opaque sliding jackets. When the slides were adjusted so that the incident light was cut off in such measure as to give equal opalescence in the two tubes, the precipitate was taken as inversely proportional to the lengths exposed to the light. This relation does not hold accurately for dense precipitates, since the nearer portion partly hides the more distant ones; but for slight opalescence the error is not great, especially when the lengths are not very different. With care, considerable accuracy could be attained, but to secure good results, long practice was necessary.

In order to reduce the uncertainty of comparison due to the inevitable distance between the centers of the two test-tubes, this instrument has been modified and improved. In its present form the instrument is shown in the figure on the following page. There are three separate parts, the main frame A, which holds the tubes in position, a movable top B, containing adjustable prisms, and a large box C, in which is a source of light.

The tubes destined to hold the solutions under examination were test-tubes of clear glass free from striations, and containing each 0.032 liter, painted outside around the top and bottom with black asphalt paint. These opaque bands form the most convenient method of obliterating reflections from the meniscus and the curved bottom of the test-tube. The space between the lower edge of the upper band and the bottom of the tube was exactly the same in each case. The lower edge of the upper band projected below the wooden support, P, in order to provide a sharp line of demarcation between light and darkness, as well as to allow the tubes to be shut into complete darkness by the sliding jackets, S,S. The tubes rested upon equal wooden pillars (which guided the sliding jackets) and projected well above the support, P, in order to preserve their cleanliness. The sliding jackets were also of glass, thickly painted. They moved up and down over the test-tubes, shutting off as much light as was wished and being held in any desired place by a brass spring. When raised, they disclosed below two scales which indicated exactly the lengths of the tubes above exposed to the light.



Upon the frame rested the small box B, which shut out all light, and yet was easily removable. In this box was a small frame which could be adjusted to any position by means of the set screw R. This frame contained two 15° prisms with their thin edges together, the edges having been ground slightly by an optician until they fitted closely. The effect of the prisms when looking downwards through them is to bring into view, side by side, semicircular images of about half of each tube, so that the two halves appear scarcely larger than a single tube, the dividing line being barely visible. The appearance of the image resembles the field of a half-shadow

polarimeter. The success of the instrument lies in this arrangement of the prisms. Different observers can judge the equality of two tubes to within a few per cent, an accuracy impossible with the older nephelometer where the mind had to estimate the small differences at a distance; under favorable conditions successive readings of the scale by one observer will not vary so much as a millimeter.

For stirrers, propeller-shaped pieces of platinum foil were sealed upon two glass rods. These stirrers seemed to insure a more efficient mixing with less danger of contamination than the process of decanting back and forth between two tubes, as recommended by Stas. They were always kept standing in separate tubes of pure water when not in use.

The apparatus was thoroughly tested by comparing with its aid solutions containing known amounts of freshly precipitated argentic chloride in suspension. Its efficiency is most easily seen in a series of results where portions of the same opalescent liquid were placed in the two tubes for comparison. This procedure obviates any possible inconsistency arising from unequal speed of precipitation—a matter to be discussed in a subsequent paper.

In the manipulation the most scrupulous care must be taken to avoid the introduction of dust, which usually contains chloride enough to affect the test. Hydrochloric acid gas is also an insiduous source of contamination. The tubes were filled until the meniscus rose above the upper blackened rim, and were then placed in a light-shield,—a large box blackened inside. The outer surfaces of the tubes were always wiped with a very clean cotton cloth, and the incandescent electric light used as a source of illumination was only turned on during the few minutes required for the readings. During this short time no sensible darkening of the precipitate occurs, since the light is deficient in violet and ultraviolet rays.

Below are given the results obtained with three pairs of tubes, each containing an opalescent liquid with 2 milligrams of argentic chloride suspended in a liter of solution. The suspension of this small amount of substance had been effected

by adding a considerable excess of argentic nitrate to a suitable solution of chloride, which is thus practically all precipitated.

Comparison of Similar Solutions.

	Heights of equal intensity. Tube *a*.	Tube *b*.	Ratio $\frac{a}{b}$.
	mm.	mm.	
Pair 1	53	52	1.02
	53	55	0.96
	53	53.5	0.99
		Average,	0.992
Pair 2	53	51	1.04
	53	54	0.98
	53	55	0.96
		Average,	0.997
Pair 3	53	56	0.95
	53	51	1.04
	53	54	0.98
	77	77	1.00
	34.2	34.2	1.00
	67	64	1.05
		Average,	100.3

Total average, 0.998 ± 0.001

The close agreement of these readings shows the absence of any constant error greater than 1 per cent either in the prisms, the tubes, the lighting, or the scale. Evidently, too, the length of the tube exposed to the light makes no difference; but, nevertheless, in practice, settings were usually made at several different heights. The actual error (0.2 per cent) of the mean of the twelve settings corresponds to only 0.00005 milligram of argentic chloride, and the maximum deviation (5 per cent) of a single observation from the true value corresponds to 0.0015 milligram. Thus the instrument is capable of a considerable degree of accuracy.

To determine the soluble chloride in an unknown solution—for example, the filtrate from a large mass of precipitated argentic chloride—suitable volumes of a known standard solution and of the unknown solution, were made up to equal volumes in the respective tubes. A milliliter of the standard

solution of sodic chloride used for this particular comparison was equivalent to 0.00526 milligram of silver chloride. To preserve it from contamination it was kept in a large bottle with a burette attached, out of all contact with the outside air, save through a tube containing cotton wool. The unknown solution was always introduced into the right-hand tube of a pair by means of a pipette, to the left-hand tube was added the desired volume of standard solution, and then pure water was added to each. After stirring, a milliliter of a solution of silver nitrate, equivalent to 1 milligram of silver, was added to both tubes. Stirring shortens the time required for precipitation, but care must be used that no minute spatterings spring from one tube to the other. Even then, long time is required to attain complete precipitation, two hours at least being needed for comparative accuracy, and as much as fifteen hours for the greatest precision of which the method is capable. The presence of an electrolyte, such as nitric acid or sodic nitrate, greatly accelerates the passage from the colloidal to the solid condition, and lessens the time required. Since this question concerns rather the mechanism of a particular reaction than the working of the apparatus, the detailed discussion of our results in this direction will be reserved for a future paper.

Since a small trace of accidentally admitted chloride so profoundly vitiates the result the greatest care is necessary in every step of the operation. Even the distilled water of the laboratory sometimes showed traces of chloride, if it had stood long in unstoppered flasks. All the substances used in these experiments (except the standard solution of salt) were completely free from traces of chloride, and all apparatus connected with the work was kept unusually clean with large quantities of redistilled water. The purest water was redistilled into a large bottle, through a special adapter for excluding dust. When the adapter was removed, a tube containing soda replaced it so that no trace of hydrochloric acid from the air could enter the bottle when water was withdrawn through a siphon. It is to be noted that hydrochloric acid almost always exists in the atmosphere of a laboratory in which bottles of the solution are kept.

Below are given three typical experiments determining the quantity of silver chloride found in a certain solution according to the method described above.

	Standard solution. Milliliters.	Unknown solution. Milliliters.	Ratio of the scale readings.	Silver chloride per liter found. Milligram.
Exp. 1	5.00	10.00	0.85	2.24
" 2	4.40	10.00	1.01	2.29
" 3	4.30	10.00	0.99	2.24
				2.26

These results illustrate sufficiently the degree of accuracy which may be easily obtained, as well as the best method of proceeding. The first comparison is made with solutions only approximately equal, and the succeeding observations are made upon tubes containing quantities of substance, computed from the first trial, which are much more nearly equal. In this way the greatest accuracy may be reached.

The instrument may be used similarly in many other cases when a finely divided precipitate reflects light, and provides an unusually sensitive means of detecting very faint cloudiness in a liquid. Care must be taken to have both standard solution and unknown solution subjected to precisely the same conditions, for varying conditions of precipitation may lead to differences in the appearance of the precipitate far greater than the possible optical error of the apparatus. Herein lies the chief caution to be noted in its use. By modifying the apparatus in such a way as to provide a bright background, the arrangement might be a very convenient device for the colorimetric comparison of transparent liquids.

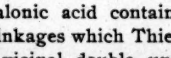
The contents of this paper may be summarized as follows: An instrument for the comparison of opalescent mixtures is described, the essential advantage of which lies in the optical juxtaposition of the fields of view to be compared, by means of prisms. This improvement over the earlier nephelometer increases the ease and accuracy of the setting. The instrument, thus improved, is able to detect and estimate very small amounts of suspended precipitate. The chief possi-

bility of error lies in the state of the precipitated material. In order to exclude variation here, the solution to be estimated and the standard solution for comparison should be precipitated in exactly the same way.

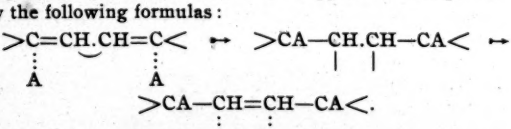
THE ADDITION OF ACID SULPHITES TO CINNAMYLIDENEMALONIC ACID.

By Elmer P. Kohler.

Cinnamylidenemalonic acid contains the combination of single and double linkages which Thiele has called a "conjugated system of vicinal double unions."[1] According to Thiele such a system should be represented by the general formula



in which the dotted lines denote "partial valences." When a substance that has this kind of a chain combines with a molecule of another substance the combination is supposed to take place through the partial valences, and the successive steps in the process of addition are supposed to be represented by the following formulas:

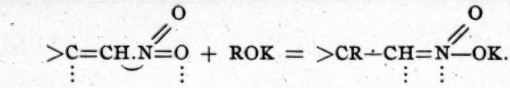


This view can be tested by determining the structure of the product. If addition takes place as here represented, then the product must have the addends in combination with the carbon atoms at the extremities of the conjugated system, and a new "active" double linkage in the middle. Thiele and others have shown that this is undoubtedly true in a number of cases in which the addends are of the same kind, as, for example, two hydrogen atoms or two bromine atoms.

It is not so well established that combination may take place in this way when the addends are not of the same kind.

[1] Ann. Chem. (Liebig), 306, 94.

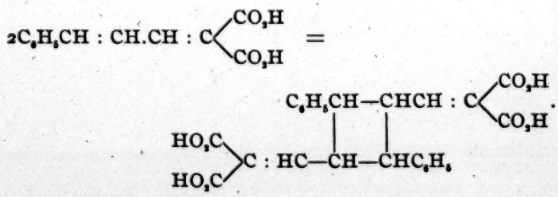
Meisenheimer[1] and Thiele[2] have recently found a plausible explanation for the peculiar behavior of some nitro compounds by assuming that an alcoholate can combine at the ends of a conjugated system as follows:



It is difficult, however, to establish the structure of metallic derivatives like these, and no case is known where dissimilar addends combine at the ends of a conjugated system composed entirely of carbon atoms.

While studying the action of light on cinnamylidenemalonic acid,[3] I found that the substance combines with acid sulphites in the cold. Since the aliphatic sulphonic acids are stable, well-defined substances there seemed to be an opportunity, here, for studying the addition of dissimilar groups to conjugated systems. One case of direct addition to the acid has already been described. Thiele and Meisenheimer[4] found that when the methyl ester of the acid combines with 1 molecule of hydrocyanic acid, the cyanogen group goes into the β-position instead of into the Δ-position as they had anticipated. This addition, therefore, involves only the double union nearest the carboxyl groups.

It has also been shown[5] that in direct sunlight the acid rapidly goes into a tetramethylene derivative:



[1] Ann. Chem. (Liebig), 323, 205.
[2] *Ibid.*, 325, 1.
[3] This JOURNAL, 28, 239.
[4] Ann. Chem. (Liebig), 306, 247.
[5] Ber. d. chem. Ges., 38, 2411.

This change, which is essentially one of addition, involves only the double union nearest the phenyl group.

The results described below show that when the acid combines with 1 molecule of an acid sulphite, the sulphoxyl group goes into the β-position. The structure of the resulting product was established by the following reactions.

When a solution of the neutral potassium salt that is obtained as the direct product of addition is acidified, an unstable acid salt is precipitated:

$$C_6H_5CH : CHCHCH\begin{matrix}CO_2K\\CO_2K\end{matrix} + 2HCl =$$
$$\begin{matrix}\\SO_3K\end{matrix}$$

$$C_6H_5CH : CHCHCH\begin{matrix}CO_2H\\CO_2H\end{matrix} + 2KCl.$$
$$\begin{matrix}\\SO_3K\end{matrix}$$

This, on heating, loses carbon dioxide:

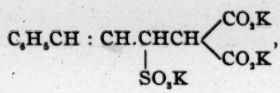
$$C_6H_5CH : CHCHCH\begin{matrix}CO_2H\\CO_2H\end{matrix} = C_6H_5CH : CHCHCH_2CO_2H.$$
$$\begin{matrix}\\SO_3K\end{matrix} \qquad\qquad \begin{matrix}\\SO_3K\end{matrix}$$

The resulting acid salt is oxidized to benzaldehyde, carbon dioxide, and β-sulphopropionic acid:

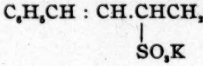
$$C_6H_5CH : CHCHCH_2CO_2H + 3O =$$
$$\begin{matrix}\\SO_3H\end{matrix}$$

$$C_6H_5CHO + \left[\begin{matrix}CO_2HCHCH_2CO_2H\\\\SO_3H\end{matrix}\right] \rightarrow \begin{matrix}CH_2CO_2H\\|\\CH_2SO_3H\end{matrix} + CO_2.$$

When an aqueous solution containing molecular quantities of acid potassium sulphite and cinnamylidenemalonic acid is allowed to stand in the cold the sulphite slowly diminishes in quantity, and at the end of four or five days the solution no longer gives a reaction for sulphites. The liquid then contains two salts—the potassium salt of benzalsulphoethylmalonic acid,



and the potassium salt of benzalsulphobutyric acid,



By warming a similar solution on the water-bath the same change may be completed in half an hour.

The same two salts are obtained when potassium sulphite is added to a solution of the acid potassium salt of cinnamylidenemalonic acid, and when sulphur dioxide is slowly passed into a solution containing potassium sulphite and the neutral salt of the unsaturated acid. These salts crystallize only from very concentrated solutions, and it was not possible to separate them from each other by systematic fractional crystallization of the mixture. It was found, however, that the salt of benzalsulphoethylmalonic acid is less soluble in a strong solution of potassium hydroxide than the salt of benzalsulphobutyric acid, and a method of separation was based on this difference.

The Potassium Salt of Benzalsulphoethylmalonic Acid.

To prepare this salt the calculated quantity of acid potassium sulphite was added, gradually, to a hot solution obtained by neutralizing the unsaturated acid with potassium carbonate. The liquid was warmed on a water-bath until it no longer gave a yellow precipitate of unchanged unsaturated acid when acidified with dilute acids. It was then cooled in ice-water and poured into a cold solution (1 : 4) of potassium hydroxide. The shining white plates that separated were filtered off immediately, washed with a more dilute solution of potassium hydroxide, and recrystallized from water. An analysis gave the following results:

I. 0.3241 gram salt lost 0.0259 gram at 130°.
II. 0.2628 gram salt lost 0.0213 gram at 130°.
III. 0.2415 gram salt gave 0.1390 gram K_2SO_4.

IV. 0.2215 gram salt gave 0.1294 gram K_2SO_4.

	Calculated for $C_{19}H_9O_7SK_3.2H_2O$.	Found. I.	II.	III.	IV.
H_2O	7.97	8.00	8.12	....	....
K	26.06	....	....	25.80	26.18

The salt is very easily decomposed. If the aqueous solution is boiled for a few hours and acidified, the yellow, unsaturated acid is precipitated, showing that the reaction

$$C_6H_5CH : CH.CH : C\begin{matrix}CO_2H\\CO_2H\end{matrix} + KHSO_3 =$$

$$C_6H_5CH : CHCH(SO_3K)\begin{matrix}CO_2H\\CO_2H\end{matrix}$$

is reversible. Solutions of alkalies split off acid sulphite in the cold. The salt is also decomposed by acids, the result depending upon the concentration of the acid. When cold, concentrated hydrochloric acid is added to a saturated solution of the salt, the solution immediately becomes yellow, and in a short time the unsaturated acid begins to separate. When dilute hydrochloric acid is added to a solution of the salt, colorless acid salts are precipitated in well-formed crystals. These acid salts are stable when dry, but they cannot be recrystallized, as they steadily lose carbon dioxide even when dissolved in cold water. Analyses of various precipitates indicated mixtures of mono- and dipotassium salts.

The Acid Potassium Salt of Benzalsulphobutyric Acid.

This salt is obtained in calculated quantity when dilute hydrochloric acid is added to a boiling solution of the neutral salt described above. It is, however, much easier to make the salt directly from cinnamylidenemalonic acid. Potassium sulphite is added, in small quantities, to the finely powdered acid suspended in boiling water. Each addition of the sulphite causes a rapid evolution of carbon dioxide. The sulphite is added until a test with dilute hydrochloric acid shows the absence of unsaturated acid. The liquid then contains the potassium salt of benzalsulphobutyric acid along with

some of the potassium salt of benzalsulphoethylmalonic acid. To remove the latter, a considerable quantity of dilute hydrochloric acid is added and the liquid warmed until a test with hot concentrated hydrochloric acid shows the absence of the salt. The sparingly soluble acid potassium salt of benzalsulphobutyric acid crystallizes from this solution on cooling. The salt is obtained in calculated quantity. It is easily purified by recrystallization from water. A potassium determination gave the following results:

I. 0.1494 gram salt gave 0.0441 gram K_2SO_4.
II. 0.2393 gram salt gave 0.0696 gram K_2SO_4.

	Calculated for $C_{11}H_{11}O_4SK$.	Found. I.	II.
K	13.30	13.23	13.10

The salt crystallizes in plates that are readily soluble in boiling water, sparingly soluble in cold water, insoluble in alcohol. It is much less easily decomposed than the potassium salt of benzalsulphoethylmalonic acid. No change could be detected when a solution in water or in dilute hydrochloric acid was boiled for eight hours. When a solution of 10 grams of the acid in concentrated hydrochloric acid was boiled for eight hours, and subsequently extracted with ether, the latter took up a small quantity of a substance which, after recrystallization from alcohol, melted at 165°. This was cinnamenylacetic acid. A similar change takes place when the salt is heated with alkalies. Five grams of the substance were dissolved in cold potassium hydroxide and the solution set aside. No sulphite could be detected in the solution after it had stood for several days. On warming the solution on a water-bath a new salt began to separate in thin, colorless plates. This was the potassium salt of cinnamenylacetic acid. The solution contained potassium sulphite.

The *neutral potassium salt* of benzalsulphobutyric acid, obtained by neutralizing the acid potassium salt with potassium carbonate, is very soluble in water. As it was not obtained in well-defined crystals it was not analyzed.

The *calcium salt* is easily obtained by neutralizing the acid potassium salt with calcium carbonate or, better, by adding a

solution of calcium chloride to a solution of the neutral potassium salt and evaporating to crystallization. It is moderately soluble in cold water, somewhat more readily in boiling water. It crystallizes in needles containing 3 molecules of water of crystallization.

I. 0.5100 gram substance lost 0.0791 gram H_2O at 140°.
II. 0.1732 gram substance gave 0.0673 gram $CaSO_4$.

	Calculated for $C_{11}H_{10}O_8SCa.3H_2O$.	Found. I.	II.
H_2O	15.54	15.50	....
Ca	11.51	....	11.43

The *barium salt* was obtained by adding a solution of barium chloride to a solution of the potassium salt. It is moderately soluble in boiling water and crystallizes from hot, saturated solutions in needles. It is partly decomposed by prolonged boiling with water.

I. 0.1548 gram salt gave 0.0922 gram $BaSO_4$.
II. 0.2122 gram salt gave 0.1258 gram $BaSO_4$.

	Calculated for $C_{11}H_{10}O_8SBa$.	Found. I.	II.
Ba	35.09	34.98	34.89

Benzalsulphobutyric acid was made from the barium salt. The barium was precipitated with a slight excess of dilute sulphuric acid, the excess of the latter removed by boiling with lead carbonate, and the lead that went into solution precipitated as sulphide. On evaporating the solution obtained in this way, the acid separated as a compact mass of colorless needles. After one recrystallization from water the acid melted sharply at 76°. An analysis gave the following results:

I. 0.2141 gram substance gave 0.4035 gram CO_2 and 0.0925 gram H_2O.

II. 0.1860 gram substance gave 0.3499 gram CO_2 and 0.0893 gram H_2O.

	Calculated for $C_{11}H_{12}O_5S$.	Found. I.	II.
C	51.53	51.46	51.31
H	4.72	4.84	4.80

The acid is not hygroscopic. It is readily soluble in water,

alcohol, and acetone; almost insoluble in ether and chloroform. It can be recrystallized from ether containing water. When heated in a capillary tube it begins to decompose, visibly, at 125° to 130°. In open vessels it slowly decomposes at the temperature of boiling water. Sulphur dioxide is given off. The residue solidifies, on cooling, to a resinous mass that is only partly soluble in a solution of sodium carbonate. From this solution acids precipitate the cinnamenylacetic acid which melts at 165°. None of the allo-acid, melting at 136°, appears to be formed.

Oxidation of Benzalsulphobutyric Acid.

The acid and its salts instantly reduce neutral, alkaline, and acid solutions of permanganates. In neutral and alkaline solutions it was impossible to get an oxidation-product that contained more than a trace of a sulphonic acid—the sulphoxyl group is split off as sulphate even when the oxidation is carried out at 0° in very dilute solution.

A solution of barium permanganate was added, drop by drop, to a solution that was kept at 0° with cracked ice. When the color of the permanganate appeared in the liquid the solution was decolorized with a small quantity of the potassium salt and filtered. The filtrate was acidified with sulphuric acid and extracted with ether. The ether, on evaporation, left only benzoic acid. The extracted liquid was digested with lead carbonate to remove the excess of sulphuric acid. A small quantity of lead that went into solution was precipitated with hydrogen sulphide and the filtrate from the lead sulphide evaporated to dryness. The potassium salts that separated contained only a trace of sulphur. Since they did not crystallize well they were turned into calcium salts by boiling with a strong solution of calcium chloride. The sparingly soluble calcium salt that separated was dissolved in hot, dilute hydrochloric acid. This solution, on cooling, deposited the characteristic crystals of acid calcium malate.

The main products obtained by oxidizing benzalsulphobutyric acid in neutral or alkaline solutions are sulphuric acid, benzoic acid, and malic acid. Since these products

show nothing with reference to the structure of the acid, it was necessary to undertake the oxidation in acid solution.

Preliminary experiments showed that in the presence of acids very little sulphuric acid is formed, even if the substance is oxidized in a boiling solution. The oxidation was, therefore, carried out as follows: A solution containing 10 grams of the potassium salt and 15 grams of phosphoric acid was heated to boiling in a flask closed with a rubber stopper with 3 holes. A glass tube connected with a steam generator passed through one of the holes, a dropping-funnel through another, and a delivery-tube, connected with a condenser, through the third. The condenser was closed by a receiver that was connected with a wash-bottle containing a solution of barium hydroxide. A solution of barium permanganate was added, drop by drop, to the liquid, which was kept boiling by a rapid current of steam. In a short time benzaldehyde began to collect in the receiver, and at the same time barium carbonate was precipitated in the wash-bottle. The addition of permanganate was continued until the purple color no longer disappeared immediately. The precipitated phosphates and oxides were then filtered off and the filtrate extracted with ether. The ether, on evaporation, left a small quantity of benzoic acid. The extracted liquid was heated to boiling and treated with a solution of barium hydroxide until the reaction was alkaline. This precipitated all of the manganese and phosphoric acid, but left a little barium in solution. After removing this in the usual way, the liquid was evaporated to small volume and allowed to cool. A very soluble potassium salt crystallized out in small, colorless crystals. After one recrystallization from water this gave the following analytical results:

I. 0.1852 gram substance lost 0.0136 gram at 135°.
II. 0.3148 gram substance lost 0.0229 gram at 135°.
III. 0.2115 gram substance gave 0.1485 gram K_2SO_4.
IV. 0.1820 gram substance gave 0.1281 gram K_2SO_4.

	Calculated for $C_6H_4SO_4K_2.H_2O$.	Found. I.	II.	III.	IV.
H_2O	7.25	7.32	7.28	....	....
K	31.52	....	....	31.50	31.61

The salt has the composition of a potassium salt of sulphopropionic acid. When a solution of the salt was boiled with a strong solution of barium chloride the characteristic barium salt of β-sulphopropionic acid separated out.

The products obtained by oxidizing benzalsulphobutyric acid are benzaldehyde, benzoic acid, carbon dioxide, and β-sulphopropionic acid. The sulphoxyl group must, therefore, be in the β-position with reference to the carboxyl group and only one double linkage is involved when acid sulphites combine with cinnamylidenemalonic acid.

The Action of Bromine on Benzalsulphobutyric Acid.

When a drop of bromine is added to a moderately concentrated, cold, aqueous solution of the acid a blood-red, amorphous precipitate separates while the liquid remains colorless. In contact with the liquid, the precipitate immediately begins to lose its color. The liquid first becomes milky, then clears up again and a colorless substance crystallizes out in very small, lustrous crystals. If these crystals are allowed to remain in contact with the liquid they slowly disappear, and in the course of a few hours the liquid becomes as clear as it was at the beginning. This process may be repeated until the solution contains 2 atoms of bromine for every molecule of unsaturated acid. After that the bromine remains unchanged.

Similar changes take place when bromine is added to aqueous solutions of the salts of the acid. In solutions of the acid potassium, acid sodium, and acid ammonium salts bromine produces a red precipitate provided the concentration exceeds 1 part of salt in about 100 parts of the solution. If the concentration is less than this and greater than 1 part of salt in about 1500 parts of water, the colorless substance crystallizes out without the intermediate precipitation of the red substance. In still more dilute solutions the bromine is decolorized without the formation of a precipitate.

In aqueous solutions of the neutral potassium, calcium, and barium salts, bromine also produces a red precipitate, provided the solutions contain at least 1 part of salt in 250 parts of

water. In more dilute solutions the bromine is rapidly decolorized, but no precipitate forms. When the resulting solutions are acidified the same colorless substance obtained in the preceding cases crystallizes out.

The red precipitate obtained in all these cases seems to be a peculiar addition-product of 2 atoms of bromine to a molecule of benzalsulphobutyric acid or a molecule of one of its salts. I have not as yet succeeded in getting a pure substance from any of the solutions. The precipitate formed from the acid is so unstable that most of it becomes colorless before it can be removed from the liquid. It does not form in the absence of water and does not exist in solution. The precipitates formed from salts are more stable than that formed from the acid. A rough comparison gave the following results: The precipitate formed from a solution of 0.02 gram-molecule of the acid in 20 cc. of water completely lost its color in twenty minutes, that from 0.02 gram-molecule of the acid potassium salt in two weeks, and that from 0.02 gram-molecule of the neutral potassium salt in about three months. When these precipitates are rapidly dried in a vacuum or on drying plates they apparently retain their color indefinitely, but no two preparations give the same analytical results. In appearance and general properties the substances resemble the oxonium compounds of unsaturated ketones, etc. For the present their structure remains unknown.

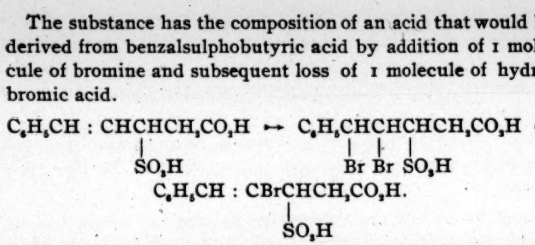
The colorless substance obtained by adding bromine to dilute solutions of benzalsulphobutyric acid was dried on filter-paper and recrystallized from ether. A qualitative analysis showed the presence of sulphur and bromine, and combustions gave the following results:

I. 0.2424 gram substance gave 0.3494 gram CO_2 and 0.0693 gram H_2O.

II. 0.2919 gram substance gave 0.4220 gram CO_2 and 0.0840 gram H_2O.

	Calculated for $C_{11}H_{11}BrO_3S$.	Found. I.	Found. II.
C	39.30	39.39	39.44
H	3.28	3.18	3.19

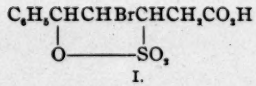
The substance has the composition of an acid that would be derived from benzalsulphobutyric acid by addition of 1 molecule of bromine and subsequent loss of 1 molecule of hydrobromic acid.



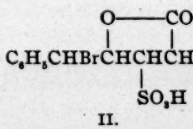
It appeared highly improbable, however, that a sulphonic acid of this structure would not be more soluble than 1 part in 1500 parts of water. It seemed much more likely that the substance is a sultonic acid analogous to the lactonic acids that are formed by the action of bromine on β,γ-unsaturated dibasic acids. The basicity determinations pointed in the same direction, since they showed that the substance is a monobasic acid that becomes dibasic when warmed with alkalies. The results are as follows:

In the cold, 0.1645 gram substance neutralized 0.0194 gram sodium hydroxide instead of 0.0192 gram calculated for a monobasic acid; and 0.1742 gram substance neutralized 0.0199 gram sodium hydroxide instead of 0.0208 gram calculated. When warmed with an excess of sodium hydroxide 0.1825 gram substance neutralized 0.0415 gram sodium hydroxide instead of 0.430 gram calculated for a dibasic acid.

When the substance is dissolved in boiling water and then neutralized, the amount of base required lies between the amounts calculated for a monobasic and a dibasic acid. A monobasic acid, with the composition of the substance under consideration, may be either a sultonic acid or a lactonic acid, as shown by the following formulas, which represent two out of a number of possibilities:



I.



II.

It is easy to decide between two formulas like these, since a substance with the structure represented by I. should form stable esters, while the esters of sulphonic acids can be obtained only through the sulphone chlorides and are easily hydrolyzed.

The esters of the acid in question are obtained with the greatest ease and they can be hydrolyzed only by prolonged boiling with dilute acids.

The *methyl ester* was prepared by dissolving the acid in absolute methyl alcohol to which a few drops of sulphuric acid had been added, and warming the solution for a short time on the water-bath. The ester separated in crystalline form on cooling. It was recrystallized from methyl alcohol and analyzed :

0.2670 gram substance gave 0.4025 gram CO_2 and 0.0870 gram H_2O.

	Calculated for $C_{12}H_{13}BrO_5S$.	Found.
C	41.26	41.11
H	3.75	3.62

The ester melts at 148°. It is readily soluble in chloroform, ether, and in boiling alcohol; moderately soluble in cold alcohol and in ligroin; insoluble in water. It crystallizes in large, colorless prisms.

The *ethyl ester* very closely resembles the methyl ester. It melts at 121°.

0.2166 gram substance gave 0.3398 gram CO_2 and 0.0806 gram H_2O.

	Calculated for $C_{13}H_{15}BrO_5S$.	Found.
C	42.97	42.76
H	4.13	4.13

These results suffice to show that the substance is a sultonic acid, but they do not prove that the sultone ring is closed in the γ-position as represented; nor do they show the location of the halogen atom. The substance has been transformed in a variety of different ways but the results cannot

be interpreted definitely until these points are established. They will, therefore, be reserved for a later paper.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
November, 1903.

THE ADDITION OF IODINE AND POTASSIUM IODIDE TO ORGANIC COMPOUNDS CONTAINING THE CARBONYL GROUP.

BY A. M. CLOVER.

When iodine, potassium iodide, and benzophenone are brought together in solution, and the solvent removed by evaporation, the residue contains a crystalline substance of a golden luster. When the three substances are melted together and the product allowed to cool, a crystalline residue of the same appearance is obtained.

The compound just mentioned may be obtained in a pure state by recrystallizing the crude product from ether or chloroform. If an excess of iodine has been used, this must be removed by pulverizing the crude product and allowing it to remain in a vacuum: otherwise the iodine is dissolved by the solvent and crystallizes out with the compound. It is more convenient, however, to use an excess of the other constituents, as these are completely separated from the compound on recrystallizing.

The compound was found to consist of iodine, potassium iodide, and benzophenone, each of which may be recovered unchanged. The crystals are very soluble in acetic ether, acetic acid, and acetone; moderately soluble in chloroform, ether, and alcohol, and sparingly soluble in benzene, carbon disulphide, and ligroin. In dilute solution the substance is dissociated into its constituents. When the crystals are shaken with benzene, the iodine and benzophenone gradually go into solution and the potassium iodide is deposited as a residue. The crystals melt at about 100°, and above this point the vapor of iodine may be detected. When shaken with water they are slowly dissociated, the iodine and potassium iodide going into solution and the benzophenone being

left as a residue. This change is hastened by the addition of an immiscible solvent such as chloroform.

It was found that the crystals obtained have the same composition, regardless of the proportion in which the constituents are brought together. If an excess of benzophenone was used, this remained in the mother-liquor on recrystallizing. An excess of potassium iodide remained as a residue on dissolving the crude product. An excess of iodine was removed in a vacuum or by dissolving the compound in a small amount of acetic ether, filtering from excess of iodine and potassium iodide, and then removing the solvent by evaporation in a vacuum.

The substance was finally prepared by mixing 8 parts of benzophenone with 4 parts of iodine and 3 parts of potassium iodide. The mixture was warmed to 100° and the melted product stirred for several minutes. It was then poured into a dish and allowed to cool. The solid product was then pulverized and recrystallized from ether or chloroform by dissolving at ordinary temperature and cooling in a freezing-mixture. The crystals obtained were filtered without suction and then packed together tightly on a porous plate in order to remove all mother-liquor. The crystals obtained from chloroform were found to have a slightly different composition from those out of ether. This difference is due to the fact that in each case the solvent enters into the compound. In each case the crystals are hexagonal prisms whose sides have a golden luster and whose bases are dark-blue. Those from chloroform are much larger and better defined.

Methods of Analysis.

(1) The iodine was estimated by covering the substance with a solution of potassium iodide, adding a few drops of chloroform, and shaking until the compound was completely dissociated. The solution was then titrated with a standard solution of sodium thiosulphate.

(2) The potassium iodide was estimated by determining the total iodine in the compound and subtracting from this

the free iodine obtained in (1). The total iodine was estimated by covering the substance with 10 cc. of a saturated aqueous solution of sulphur dioxide, in a small flask, warming slightly, and shaking until the color of iodine had entirely disappeared. The contents of the flask were then cooled and the benzophenone pulverized with a glass rod. The solution was then carefully filtered and the iodine determined by means of standard solutions of silver nitrate and ammonium thiocyanate.

(3) The benzophenone was determined by direct weighing after the removal of the other constituents. The substance was placed in a small flask and covered with about 10 cc. of benzene. Molecular silver was then added and the contents of the flask warmed gently and shaken until the iodine had been completely removed. The benzophenone dissolved in the benzene was then carefully and completely removed from the flask and filtered into a dish from which the solvent was then removed by evaporation in a vacuum. Preliminary experiments with known quantities of benzophenone showed that it could be accurately estimated in the presence of the other two substances by this method.

Substance Crystallized from Chloroform.—After drying on a porous plate, the crystals are contaminated with a small amount of uncombined iodine. This may be completely removed by allowing them to remain in a vacuum for two hours with frequent agitation. After this time the substance continues to lose weight at a uniform rate in a vacuum and much slower at ordinary pressure. For analysis, the substance was allowed to remain in a vacuum for two hours. The loss in weight of the pure substance, in this time, is inconsiderable.

Sample 1 :

0.2714 gram substance required 12.67 cc. N/20 thiosulphate.

0.2715 gram substance required 16.25 cc. N/20 silver nitrate.

Sample 2 :

0.2501 gram substance required 11.7 cc. N/20 thiosulphate.

0.3387 gram substance required 20.32 cc. N/20 silver nitrate.

Sample 3:

0.2933 gram substance required 13.58 cc. N/20 thiosulphate.

0.2303 gram substance required 10.69 cc. N/20 thiosulphate.

0.2004 gram substance required 11.92 cc. N/20 silver nitrate.

0.2844 gram substance gave 0.1562 gram benzophenone.

0.3051 gram substance gave 0.1687 gram benzophenone.

Sample 4, crystallized twice:

0.3291 gram substance required 15.4 cc. N/20 thiosulphate.

Determination of the total halogen in the compound, by the method of Carius, gave results much higher than those obtained above. From these results it was concluded that the substance contains chloroform of crystallization.

Sample.	Free iodine. Per cent.	Total iodine. Per cent.	Benzophenone. Per cent.
1	29.58	37.93	....
2	29.67	38.05	....
3	{ 29.32 { 29.46	37.70	{ 54.92 { 55.29
4	29.68	....	....
Average,	29.58	37.89	55.10

Potassium iodide, by difference, 10.88 per cent.

Total iodine, potassium iodide, and benzophenone, 95.56 per cent.

Combining ratio between iodine and potassium iodide, $\frac{7.11}{2}$.

Combining ratio between benzophenone and potassium iodide, $\frac{9.22}{2}$.

The three constituents are therefore combined in the ratio of 9 : 7 : 2. The substance contains 1 molecule of chloroform and is represented by the formula $(C_{18}H_{10}O)_9(KI)_2I_7,CHCl_3$.

	Calculated.	Found (by difference).
Chloroform	4.01	4.44

Substance Crystallized from Ether.—The crystals obtained from ether contain only a trace of uncombined iodine, for samples analyzed immediately after drying did not show a

much higher percentage of iodine than those which had remained in a vacuum for an hour or more. The substance loses in weight slowly on standing in a desiccator at ordinary pressure and more rapidly in a vacuum. One gram substance lost 3 milligrams in weight on standing for three days in a desiccator at ordinary pressure. The loss in weight is probably due to loss of ether of crystallization rather than iodine, for an analysis of this sample made at the end of ten days showed no loss in the percentage of iodine.

Sample 1, crystallized twice :

0.2831 gram substance required 13.55 cc. N/20 thiosulphate.

Sample 2 :

0.2562 gram substance required 12.36 cc. N/20 thiosulphate.

0.2961 gram substance required 18.24 cc. N/20 silver nitrate.

0.2470 gram substance required 15.32 cc. N/20 silver nitrate.

Sample 3 :

0.2325 gram substance required 11.28 cc. N/20 thiosulphate.

0.2980 gram substance gave 0.1662 gram benzophenone.

0.2914 gram substance gave 0.1626 gram benzophenone.

Sample.	Free iodine. Per cent.	Total iodine. Per cent.	Benzophenone. Per cent.
1	30.34	....	....
2	30.60	39.07 39.33	....
3	30.77	....	55.77 55.79
Average,	30.57	39.20	55.78

Potassium iodide, by difference, 11.29 per cent.

Total iodine, potassium iodide, and benzophenone, 97.64 per cent.

Combining ratio between iodine and potassium iodide, $\frac{7.08}{2}$.

Combining ratio between benzophenone and potassium iodide, $\frac{8.9}{2}$.

The compound evidently contains ether of crystallization and is represented by the formula $(C_{18}H_{10}O)_8(KI)_2I_7,C_4H_{10}O$.

	Calculated.	Found (by difference).
Ether	2.52	2.36

It will be noted that, disregarding the solvent, the formulas of the crystals obtained from the two solvents are the same.

Benzoic Anhydride Compound.

Benzoic anhydride forms a compound very similar to the one just described. It has a high luster, the shade of which lies between a golden and a steel-gray. The crystals are deposited from solution in the form of a stringy mesh, from which it is very difficult to remove the solvent. The substance is much more stable than the benzophenone compound. As in the previous case, it was found that regardless of the proportion in which the constituents were brought together, the purified product had always the same composition. The crude product was most easily prepared by melting together 13 parts of benzoic anhydride with 6 parts of iodine and 3 parts of potassium iodide. It may also be obtained by adding a strong solution of iodine in potassium iodide to a solution of the anhydride in acetic acid, the compound being precipitated.

An excess of either of the constituents in the crude product was removed in the manner already described under the benzophenone compound. The substance has about the same solubilities as the benzophenone compound except that it is only sparingly soluble in ether and chloroform. It is also dissociated in very dilute solution. It is best purified by recrystallizing in a freezing-mixture from absolute alcohol or from a mixture of equal volumes of acetic ether[1] and chloroform. The crystals are less difficult to filter if the solution be agitated during the crystallization.

For analysis, the substance was filtered with suction and pressed out on a porous plate, finally to a powder. It then remained in a vacuum for four or five hours, having been frequentlyrepulverized. It was found that the substance obtained from either solvent continued to lose in weight slowly in a vacuum and more slowly in a desiccator at ordinary pressure.

Three grams substance from absolute alcohol lost 1 milligram after being twelve hours in a vacuum.

[1] The acetic ether used here and in other parts of this work was anhydrous and free from alcohol.

Two and five-tenths grams substance from acetic ether-chloroform lost 0.7 milligram after eighteen hours in a desiccator at ordinary pressure.

The substance melts at 125° to 128°; there is no noticeable dissociation of iodine below this point.

Samples of the substance purified by both methods were analyzed. The estimation of the constituents was made in the same way as with the previous compound, except that in the estimation of anhydride a small amount of acetic ether was used with the benzene as the compound is almost insoluble in pure benzene. Careful tests showed that benzoic anhydride could be accurately estimated in the presence of iodine and potassium iodide by this method.

Sample 1, crystallized from acetic ether and chloroform:

0.2982 gram substance required 13.8 cc. N/20 thiosulphate.

0.3320 gram substance required 15.35 cc. N/20 thiosulphate.

0.3321 gram substance required 20.9 cc. N/20 silver nitrate.

0.2601 gram substance required 16.35 cc. N/20 silver nitrate.

0.2943 gram substance gave 0.1669 gram benzoic anhydride.

0.2779 gram substance gave 0.1576 gram benzoic anhydride.

Sample 2, crystallized from absolute alcohol:

0.3042 gram substance required 14.16 cc. N/20 thiosulphate.

0.2791 gram substance required 17.6 cc. N/20 silver nitrate.

0.2633 gram substance required 16.7 cc. N/20 silver nitrate.

0.3415 gram substance gave 0.1928 gram benzoic anhydride.

0.4105 gram substance gave 0.2324 gram benzoic anhydride.

Sample 3, crystallized from absolute alcohol:

0.3243 gram substance required 14.9 cc. N/20 thiosulphate.

0.2070 gram substance required 12.93 cc. N/20 silver nitrate.

Sample 4, crystallized from acetic ether and chloroform.

0.3109 gram substance required 14.34 cc. N/20 thiosulphate.

Sample.	Free iodine. Per cent.	Total iodine. Per cent.	Benzoic anhydride. Per cent.
1	{ 29.35 { 29.30	{ 39.92 { 39.84	{ 56.71 { 56.71
2	29.52	{ 39.96 { 40.22	{ 56.45 { 56.61
3	29.14	39.58	....
4	29.25	....	....
Average,	29.31	39.85	56.62

Potassium iodide, by difference, 13.79 per cent.

Total iodine, potassium iodide, and benzoic anhydride, 99.72 per cent.

Combining ratio between iodine and potassium iodide, $\frac{2.78}{1}$.

Combining ratio between benzoic anhydride and potassium iodide, $\frac{3.01}{1}$.

If the substance has the composition $(C_{14}H_{10}O_3)_3, KI, I_3$, the product obtained is not pure. As the analysis of different samples gave practically the same figures and as the total of constituents, found, amounts to almost 100 per cent, it is quite probable that the product is pure and accordingly the simplest formula to be assigned is $(C_{14}H_{10}O_3)_{13}, (KI)_4, I_{11}$.

A determination of the molecular weight by the cryoscopic method was deemed useless on account of the known tendency of these substances to dissociate in solution.

Phthalic Anhydride Compound.

For the preparation of this compound an excess of phthalic anhydride was melted with iodine and potassium iodide. The product solidified, on cooling, to a highly lustrous, green, crystalline mass, which was pulverized. The compound was dissolved away from the excess of anhydride by means of a small amount of acetic ether. The filtered solution was then treated with 3 volumes of chloroform and the compound obtained by crystallizing in a freezing-mixture.

When excess of iodine was used in the preparation it was removed in a vacuum, and the compound purified in the same way had the same composition as in the previous case.

The crystals were filtered without suction and then packed tightly on a porous plate to remove all mother-liquor. They then remained in a vacuum for four or five hours before analysis. When kept in a vacuum for some time, the crystals on top lose their luster, showing dissociation, but the loss in weight is inconsiderable.

Two grams lost 0.6 milligram, in a vacuum for three hours.

The same sample lost 0.4 milligram after standing sixteen hours in a desiccator at ordinary pressure.

The substance is only sparingly soluble in chloroform and ether. It is moderately soluble in alcohol, but is dissociated, anhydride separating out.

When added to water it soon dissociates, all of the products going into solution.

The crystals are fine and irregular in shape. They are dark-green in color and have a beautiful luster.

Sample 1:

0.2854 gram substance required 23.44 cc. N/20 thiosulphate.

Sample 2:

0.2447 gram substance required 20.1 cc. N/20 thiosulphate.

0.2038 gram substance gave 0.1479 gram CO_2 and 0.0165 gram H_2O.

Sample 3:

0.3291 gram substance gave 0.3964 gram AgI (substance dissolved in water and iodine reduced with sulphur dioxide).

0.2698 gram substance required 22.1 cc. N/20 thiosulphate.

Sample 4:

0.1970 gram substance required 16.09 cc. N/20 thiosulphate.

0.2408 gram substance required 24.7 cc. N/20 silver nitrate.

0.2159 gram substance gave 0.1550 gram CO_2 and 0.0166 gram H_2O.

Sample.	Free iodine. Per cent.	Total iodine. Per cent.	Anhydride. Per cent.
1	52.09	....	....
2	52.11	....	30.60
3	51.95	65.08	....
4	51.77	65.05	30.25
Average,	51.98	65.06	30.42

Potassium iodide, by difference, 17.12 per cent.

Total iodine, potassium iodide, and phthalic anhydride, 99.52 per cent.

Combining ratio between iodine and anhydride, $\frac{1.99}{1}$.

Combining ratio between iodine and potassium iodide, $\frac{3.97}{1}$.

The compound is therefore represented by the formula $(C_8H_4O_3)_2KI,I_4$.

Phenylacetic Anhydride Compound.

Two grams anhydride were mixed with 2 grams iodine and 1 gram pulverized potassium iodide. The mixture was heated to 50° and stirred for several minutes. At a higher temperature the iodine seemed to act destructively upon the anhydride. The crude product was then cooled and triturated with a small amount of chloroform to dissolve out any unchanged anhydride or its decomposition-product. After filtering, the residue was placed in a vacuum for the removal of uncombined iodine. The substance was then recrystallized from chloroform and dried on a porous plate. The substance loses weight, on standing, much more rapidly than the compounds previously described. The analyses were therefore made soon after the substance had been prepared and allowed to remain in a vacuum for a few minutes.

One and one-tenth grams substance remained in vacuum for three-fourths of an hour and was found to have lost 8 milligrams.

The same sample then lost 16 milligrams, after seven hours, in a desiccator at ordinary pressure.

The loss in weight is continuous and is due to combined iodine, as the substance has the odor of iodine and free iodine was noted in the containing vessel after standing for some time.

The substance is very soluble in ether, alcohol, acetic ether, and acetone; moderately soluble in chloroform; insoluble in benzene.

The analyses were made in the same way as those of the

benzophenone and benzoic anhydride compounds. In the estimation of total iodine concordant results could not be obtained. The per cent of potassium iodide was, therefore, found by difference, assuming that the substance contains no solvent.

Sample 1 :

0.2331 gram substance required 18.97 cc. N/20 thiosulphate.

0.2652 gram substance required 21.48 cc. N/20 thiosulphate.

Sample 2 :

0.1459 gram substance required 11.9 cc. N/20 thiosulphate.

0.1678 gram substance required 13.7 cc. N/20 thiosulphate.

0.2727 gram substance gave 0.0961 gram phenylacetic anhydride.

0.4281 gram substance gave 0.1479 gram phenylacetic anhydride.

Sample 3 :

0.1724 gram substance required 14.15 cc. N/20 thiosulphate.

0.2502 gram substance gave 0.0875 gram phenylacetic anhydride.

0.2110 gram substance gave 0.0748 gram phenylacetic anhydride.

Sample.	Free iodine. Per cent.	Anhydride. Per cent.
1	51.62	....
	51.37	....
2	51.73	35.24
	51.78	34.55
3	52.09	34.97
		35.40
Average,	51.77	34.78

Potassium iodide, by difference, 13.45 per cent.

Combining ratio between iodine and anhydride, $\frac{2.98}{1}$.

Combining ratio between iodine and potassium iodide, $\frac{5.04}{1}$.

The simplest formula to be assigned to this substance is, therefore, $(C_{18}H_{14}O_4)_5,(KI)_3,I_{18}$.

Succinic Anhydride Compound.

This compound is less stable and more difficult to purify

than the ones previously described. When the constituents are melted together the residue solidifies, on cooling, to a golden crystalline mass.

It is in most cases impossible to obtain the crystals pure by recrystallization on account of the dissociation of the substance in dilute solution, and because of the slight solubility of the dissociated succinic anhydride in all of the organic solvents. Various solvents were tried, but only from a mixture of acetic ether and chloroform could the substance be obtained in a fair degree of purity.

Six grams succinic anhydride were melted with 4 grams iodine and 2.5 grams pulverized potassium iodide. The residue was cooled and pulverized and dissolved in about 10 cc. acetic ether and the solution filtered. Fifteen cc. chloroform were then added and the solution was again filtered. On cooling in a freezing-mixture, about 1 gram of the compound separated out. It was dried on a porous plate and kept in a vacuum ten minutes before analysis. The substance is apparently free from uncombined iodine. It loses iodine rapidly in a vacuum, but only very slowly at ordinary pressure.

0.2296 gram substance required 17.53 cc. N/20 silver nitrate.

0.2169 gram substance required 11.1 cc. N/20 thiosulphate.

Another sample was prepared in the same manner.

0.1151 gram substance required 5.45 cc. N/20 thiosulphate.

The substance is probably represented by the formula $(C_4H_4O_3)_4,KI,I_2$.

	Calculated.	Found. I.	Found. II.
Free iodine	30.9	32.46	30.03
Total iodine	46.4	48.42	....

Other crystalline anhydrides and ketones were found to form compounds similar to those described, as shown by the luster of the product obtained.

The power to form these compounds evidently depends upon the carbonyl group, which is common to anhydrides and ketones. Other substances containing this group were found to form such compounds, while with ethers, alcohols, and phenols they could not be obtained.

When benzanilide (excess) is melted with iodine and potassium iodide, the cooled product possesses a golden luster. With nitrobenzoyl chloride the same luster may be obtained, but it is less decided and may be due to the presence of nitrobenzoic anhydride as an impurity. Methyl oxalate (excess) gives a light-green luster on cooling the product. The luster disappears on warming and the compound is evidently very unstable.

Iodine and potassium iodide are together dissolved by acetone in large amounts, although singly these substances have only a small solubility in the solvent. Acetic anhydride behaves similarly to acetone. It may be concluded that compounds are formed with each of these substances, although it is impossible to isolate the compounds in these cases. With ether, however, the solubility of iodine and potassium iodide is not noticeably increased when both are present and there is no evidence of the formation of a compound. When the phenyl ether of trimethyleneglycol (the substance was selected because of its being a solid) is brought together with iodine and potassium iodide, there is no evidence of the formation of a compound.

The compounds selected for study in this work are representative ones. It was thought that possibly these compounds would be found to be of simple and uniform composition. Careful analysis, however, has shown that the composition is variable and, in most cases, complex.

LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF MICHIGAN,
ANN ARBOR, Nov. 20, 1903.

THE ACTION OF AMMONIA UPON COPPER SULPHATE SOLUTIONS.

BY JAMES LOCKE AND JACOB FORSSALL.

INTRODUCTION.

The various investigations which have recently been published on the nature of the compounds formed by treatment of a copper sulphate solution with ammonia[1] go to show that a

[1] Reychler: Bull. soc. chim., (III.), **13**, 387 (1895); Konowaloff: J. Russ. Phys. Chem. Soc., **31**, 910 (1899); Dowson and McCrae: J. Chem. Soc. (London), **77**, 1239 (1900); Gaus: Ztschr. anorg. Chem., **25**, 236.

complex radical results which contains not more than 4 molecules of ammonia to 1 atom of copper. Konowaloff, on determining the vapor-tension of the ammonia in such solutions by a dynamical method, found that for each molecule of cupric sulphate from 3.4 to 4.04 molecules of ammonia were absorbed, according to the concentrations employed. His measurements were made at 60°, on very dilute cupric solutions and with a large excess of ammonia. Reychler ascertained that the addition of 4 molecules of ammonia to 1 of cupric sulphate caused only a slight lowering of the freezing-point of the solution.

Gaus, like Konowaloff, investigated the lowering of the vapor-pressure of an ammoniacal solution produced by the addition of cupric sulphate. He used a very delicate dynamical method. In his investigation, however, he included the behavior of salts of a large number of metals in ammonia, but gives only a few determinations for each. In his two experiments with cupric sulphate and normal ammonia he found the following :

Gram-molecules Cu^{II} per liter.	Lowering of vapor-pressure. mm.
0.0491	2.49
0.0982	5.02

Assuming that ammonia solutions follow Henry's law, and adopting Gaus' value for the vapor-pressure of normal ammonia, 13.45 mm., the ratio of found ammonia to copper is given by the equation

$$\frac{l}{13.45 \cdot \mathrm{Cu}} = x,$$

where l is the lowering of the vapor-pressure and x the number of molecules in the complex. The above two determinations give, respectively, 3.77 NH_3 and 3.80 NH_3, an almost perfect agreement, although the Cu concentrations are widely different. From these two experiments Gaus drew the conclusion that the lowering of the vapor-tension of the ammonia is directly proportional to the amount of cupric sulphate added. These results have been to a certain extent confirmed

by us. The ratios of copper to total ammonia in Gaus' experiments, it may be remarked, were 1 : 20.4 and 1 : 10.2, respectively.

The investigation at hand containing the greatest number of experiments is that of Dawson and McCrae. These authors determined the distribution ratio of ammoniacal solutions containing varying quantities of both copper and ammonia, between water and chloroform, and then from the distribution constant of ammonia in aqueous solution alone, between the same media, calculated the amount of ammonia which had passed into combination in each case. They state, themselves, that the results are not very accurate, but deduce from them a mean curve, which gives the following results :[1]

Table I.

Molecules Cu^{II}.	Cu : total NH_3.	Cu : burned NH_3.
0.05	1 : 5	1 : 3.14
0.05	1 : 6	1 : 3.24
0.05	1 : 7	1 : 3.43
0.05	1 : 8	1 : 3.52
0.05	1 : 9	1 : 3.63
0.05	1 : 10	1 : 3.76
0.025	1 : 6	1 : 3.16
0.025	1 : 10	1 : 3.68
0.025	1 : 16	1 : 3.96

If, as is ordinarily assumed, but one complex, $Cu(NH_3)_4$, is formed in these solutions, the gradual change in the ratio of copper to combined ammonia here seen must be due to a change in the condition of equilibrium represented by the equation

$$Cu(NH_3)_4 = k.Cu.[NH_3]^4. \qquad (1)$$

With so wide a variation in the amount of combined ammonia, we should be able to calculate the value of the dissociation constant, k. The concentration of the complex,

$$Cu(NH_3)_4,$$

is given by

$$Cu(NH_3)_4 = \frac{NH_{3_0} - NH_{3_1}}{4},$$

[1] J. Chem. Soc. (London), 77, 1252.

where NH_{s_0} represents the total ammonia and NH_{s_1} that which has remained uncombined.

Assuming that the small quantity of residual cupric sulphate is fully dissociated, furthermore, the concentration Cu becomes

$$Cu = Cu_0 - \frac{NH_{s_0} - NH_{s_1}}{4},$$

Cu_0 being the total concentration of the copper. Substituting these values in (1), we obtain for k the expression:

$$k = \frac{NH_{s_0} - NH_{s_1}}{[4Cu_0 - (NH_{s_0} - NH_{s_1})]NH_{s_1}^4}.$$

This equation is not at all satisfied by the data of Dawson and McCrae's experiments. They give for k, values which lie anywhere between 47,000 and 1,650. According to the results of these authors (and the same applies to Konowaloff's experiments) the assumption that only one complex exists is very improbable. This becomes evident when we calculate the amount of unaltered copper sulphate presumably left in the solution. In the first experiment cited in Table I., for instance, the concentration of the residual sulphate would be:

$$0.05 - \frac{3.14 \times 0.05}{4} = 0.0105 \text{ gram-molecule per liter.}$$

We must conceive of this amount of copper, outside the complex and not precipitated by a soluble hydroxide, an assumption which is certainly very improbable.

If one complex only is formed, therefore, it must be assumed that the methods thus far employed do not give the correct value for the concentration of the residual ammonia. Either this is the case or we have to do with two complexes,

$$Cu(NH_3)_x \qquad \text{and} \qquad Cu(NH_3)_y,$$

in equilibrium according to the equation

$$Cu(NH_3)_x = k.Cu(NH_3)_y.NH_3^{x-y}.$$

In this case we obtain for k, by a process of reasoning similar to the above, the expression

$$k = \frac{x\mathrm{NH}_{3_0} - \mathrm{NH}_{3_1} - y\mathrm{Cu}_0}{[x\mathrm{Cu}_0 - (\mathrm{NH}_{3_0} - \mathrm{NH}_{3_1})]\mathrm{NH}_{3_1}^{x-y}}.$$

In this, since x and y are whole numbers, they may be found empirically from two determinations. The formula gives no satisfactory results when tested by Dawson and McCrea's data. It seemed very possible, however, that the equation would be satisfied if only measurements of greater accuracy were available, for since the calculation involves the use of differences, any errors of experiment would be much magnified in the result. The present investigation was undertaken with this object.

The method chosen was the very ingenious process devised by Gaus. It consisted in leading a known volume of electrolytic gas through the solution and then into standardized hydrochloric acid. From the fall in the conductivity of the latter, as it became partially neutralized, the amount of ammonia taken up by the gas was given, and from these data its partial pressure into the solution was calculated. The details of the method as used by us, as well as the form of the apparatus, differed somewhat from those described by Gaus, and may perhaps be advantageously described in full as a criterion of the reliability of our results. Primarily, however, the question as to how far outside influences, in addition to experimental error, interfere with the value of the data, requires discussion.

The four chief factors which may influence the degree to which the vapor-pressure of the ammonia in an ammoniacal cupric sulphate solution is lowered, are :

1. The formation of one or more complex radicals.

2. Decreased or increased solubility of ammonia in a solution of the complex, as compared with its solubility in water.

3. Double decomposition of the sulphate of the complex and ammonium hydroxide, yielding ammonium sulphate. Under this head, also, may be placed the possible formation of basic salts when the concentration of the ammonia is low.

4. Ionization of the complex radical.

Since the problem is to find only the exact amount of am-

monia which has gone to form the complex or complexes, the experimental results are entirely worthless unless we can either neglect the last three of these factors, or apply corrections for them in calculating the amount of the residual ammonia in the solutions.

The question of double decomposition (3) can probably be disregarded. There is no doubt but that the complex base, say $Cu(NH_3)_4.(OH)_2$, is very highly dissociated, and that the distribution of the acid radical between it and ammonium hydroxide would be such as to yield only a very small quantity of ammonium sulphate. Dawson and McCrea found, furthermore, that in a solution of cupric hydroxide in ammonia only 2 molecules of ammonia are absorbed for each one of the cupric compounds. This indicates that if the body $Cu(NH_3)_4(OH)_2$ were formed to any extent by the reaction,

$$Cu(NH_3)_4SO_4 + 2[NH_4 + H_2O] = Cu(NH_3)_4(OH)_2 + (NH_4)_2SO_4;$$

the secondary process

$$Cu(NH_3)_4(OH)_2 = Cu(NH_3)_2(OH)_2 + 2NH_3$$

would at once take place, and the same quantity of ammonia would thus be liberated as had been withdrawn through the double decomposition. The total amount of ammonia absorbed would thus remain constant, and in case only one complex were formed, the results would not be vitiated. If two complexes result, the calculation of the amount of each would probably be subject to a slight correction, but we have found that this is not the case. The above argument, of course, does not apply to the possible formation of basic salts when the ratio of ammonia to copper is very low. We have found that in this case the experimental results are unreliable, and they have accordingly been rejected.

The fourth factor, ionization of the complex salt, can, we think, also be disregarded. It would be noticeable only if there were a marked difference in the readiness with which the undissociated complex salt and the complex ion undergo molecular dissociation with loss of ammonia. This, however,

seems not to be the case, for Dawson and McCrae found that the addition of sodium sulphate to their solutions, which should hinder ionization, produced no change in the ratio of copper to combined ammonia.

There remains, therefore, but one disturbing factor, the possible change in solubility of ammonia in water when cupric sulphate is added to its solution. If this decreases its solubility, a given quantity of ammonia would, of course, have a higher vapor-tension in the copper solution than in water, and the ratio of combined ammonia to copper, when determined without applying any correction for this fact, would be less than the actual. This physical effect of the dissolved salt may, indeed, be relatively very great in ammoniacal solutions. Gaus found, in the case of potassium chloride, that in a 0.4 normal solution of this salt the vapor-pressure of normal ammonia was 1 mm. higher than in water alone. This corresponds to the pressure of an 0.075 normal solution of ammonia. The decrease in solubility is, therefore, about 0.19 molecule ammonia for 1 molecule of the potassium salt.

In our own experiments we believe that we have been able to estimate fairly accurately the degree to which this decrease in the solubility interferes with the experimental results, and have found that after introducing the necessary correction, the ratio of copper to combined ammonia becomes 1 : 4 in all the more dilute solutions. In other words, only the one complex, $(Cu(NH_3)_4$, results, and this is formed by virtually all the copper in the solution. An excess of ammonia is required to prevent the decomposition of this radical with precipitation of cupric hydroxide or a basic salt, but owing to the uncertain composition of the latter, the dissociation constant could not be ascertained. That all the copper in the solution passes into the complex would be expected from the behavior of such solutions toward the ordinary analytical reagents for copper, though not at all from the molecular ratios of combined ammonia to the salt, as found by either Gaus or Dawson and McCrae.

Method of Experiment.

Fig. I. shows the form of the apparatus used by us. The

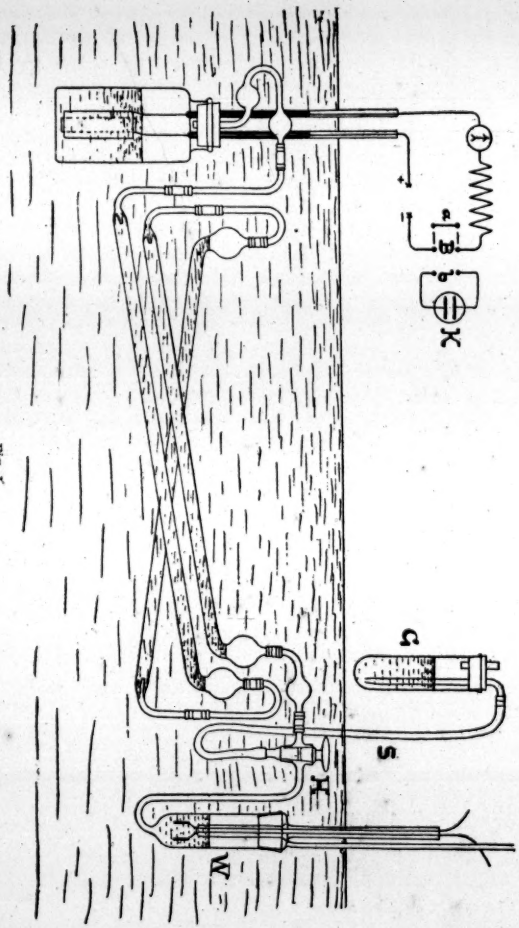


FIG. 1

absorption vessels, through which the electrolytic gas passes on its way to the resistance cell W, were obliquely held glass tubes of about 50 cc. capacity each. This seemed preferable to the arrangement of Gaus, in which they consisted of spirals of small diameter, within cylindrical bottles, the fear being that the bubbles of gas, in passing through the spirals, would be less apt to go through the ammoniacal solution than to push it before them, thus coming into actual contact with only a small quantity of the liquid. All connections were made with thick-walled rubber tubing, which was tightly ligatured with wire. Between the voltmeter and the first absorption-tube, and the last absorption-tube and resistance cell, were placed bulbs containing cotton, to prevent the respective solutions from being mechanically carried over. The resistance cell W was not surrounded by paraffin, but, as Goldschmidt[1] suggests, allowed to stand in direct contact with the water of the thermostat. It was fitted with a deep, ground-glass stopper, the joint with which was sealed by a mixture of beeswax and rosin. This stopper carried two long tubes, one of which was for the exit of the gases, the other containing the wires leading to the electrodes and supporting the latter. Contact between the wires was prevented by running one of them through a thin glass jacket. To avoid changes in the capacity of the cell through alterations in the relative position of the electrodes, with respect to the vessel itself, small marks were made upon the stopper and the rim of the cell, and these were always brought opposite each other. The amount of acid introduced into the cell was for the same reason very carefully measured, and always the same.

The current passed through the voltmeter registered at 0.5 to 1 ampere. The generation of the electrolytic gas was begun half an hour before the experiment proper, the two-way cock H during this time being so turned that the gas would pass through the tube S into G, and thence into the air. This length of time, in which to establish complete equilibrium throughout the apparatus, was found necessary for ob-

[1] Ztschr. anorg. Chem., 25, 236.

taining coincident results, although Gaus states that two minutes or so are sufficient. The tube G contained water and was employed in order to bring the gases, at the beginning of the experiment, under the same pressure as that to which they are afterward subjected. For this purpose the water column in G was of the same height as that of the hydrochloric acid in the resistance cell. Were it not for this arrangement, a certain amount of time would be required in which to overcome the pressure in the cell, and this would involve a loss.

As soon as equilibrium was secured, the experiment itself was begun. The copper cathode was immersed in the copper voltmeter K and, simultaneously, by the connection with the latter at *b* established, and the cock H so turned that the gases would pass through the capillary tube to the resistance cell. The current was allowed to flow until the resistance in W had increased to a degree indicating the neutralization of about 75 per cent of the acid by ammonia, this requiring from half an hour to an hour and a half. The experiment was then interrupted by taking out the copper cathode and turning off the cock H.

The water in the thermostat was heated by electricity. The temperature, which was regulated by an apparatus devised by Prof. W. R. Whitney, of this Institute, remained constant at 25°, the variations not being more than $\pm 0°.02$.

Calculation of the Partial Pressure of the Ammonia.—The total pressure of the mixture of gases entering the resistance cell is made up of the partial pressures.

p_1, of electrolytic gas;

p_2, of ammonia;

p_3, of aqueous vapor.

This total pressure is the same as that of the atmosphere (B_0) plus the pressure of the column of liquid in the resistance cell ($= \frac{h}{s}$, when h is the height of the liquid and s is specific gravity of Hg).

$$B_0 + \frac{h}{s} = p_1 + p_2 + p_3,$$

whence $$p_1 + p_2 = B_0 + \frac{h}{s} - p_3,$$

and $$p_2 = \frac{B_0 + \frac{h}{s} - p_3}{\frac{p_1}{p_2} + 1}. \qquad (I.)$$

Now the partial pressures of the electrolytic gas and ammonia are directly proportional to their volumes, and according to the number of gram-molecules of each (m_1 and m_2) in the mixture. For our purpose the mixture of hydrogen and oxygen may be regarded as a simple gas. We have, therefore,

$$\frac{p_1}{p_2} = \frac{m_1}{m_2}. \qquad (II.)$$

m_1, the number of gram-molecules of electrolytic gas, and m_2, that of the ammonia, are given us by the experimental data, as follows:

Notation: Cu = weight of copper precipitated in the copper voltmeter.
m = normality of the acid in the resistance cell.
V = volume of this acid, in cubic centimeters.
P = amount of the acid neutralized by the acid, in percentage.

Since 63.6 grams of precipitated copper are equivalent to 1 gram-molecule of hydrogen and 0.5 gram-molecule of oxygen,

$$M_1 = 1.5\,\frac{Cu}{63.6}.$$

The number of gram-molecules of absorbed ammonia is:

$$M_2 = \frac{P}{100} \times m \times \frac{V}{1000} = \frac{mPV}{100{,}000},$$

and therefore,

$$\frac{M_1}{M_2} = \frac{150{,}000\,Cu}{63.6\,mPV} = \frac{2358.5\,Cu}{mPV}.$$

Hence, by (I.) and (II.), the expression for p_s becomes

$$p_s = \frac{B_0 + \frac{h}{s} - p_s}{\frac{2358.5\ Cu}{mPV} + 1}.$$

p_s, the pressure of the water vapor, is not the same as that over pure water at the corresponding temperature. This is slightly lessened through the dissolved substance. The relative lowering $\frac{p-p_s}{p}$, where p = the vapor-pressure over pure water, can be approximately estimated by means of van't Hoff's formula. The correction for the copper complex formed can be neglected. With normal ammonia it amounts to about 0.42 per cent only. For the ammonia, however, it is more significant. The formula reads

$$\frac{p-p_s}{p} = \frac{1}{N},$$

in which N is the number of molecules of solvent compared with 1 molecule of the solute. If the solution is n-normal, therefore,

$$n = \frac{1000}{18.02.n} \quad \text{and} \quad p_s = p - \frac{18.02np}{1000}.$$

At 25°, the temperature at which the measurements were made, $p = 23.52$. Inserting this value, we have

$$p_s = 23.52 - 0.424n,$$

and for the complete formula,

$$p_s = \frac{B_0 + \frac{h}{s} - p + 0.01802np}{\frac{2358.5\ Cu}{mPV} + 1},$$

or at 25°,

$$p_s = \frac{B_0 + \frac{h}{s} - 23.52 + 0.424n}{\frac{2358.5\ Cu}{mPV} + 1}.$$

Gaus' formula was somewhat different. He found[1]

$$p_3 = \frac{\left(B_0 + \frac{h}{s}\right)^2}{\left(1 + 23.63\,\frac{Cu}{G}\right)\left(B + \frac{h}{s} + p\right)},$$

where G is the number of millimols of ammonia absorbed in the resistance cell. In our notation $G = \frac{mPV}{100}$, and therefore

$$p_3 = \frac{\left(B_0 + \frac{h}{s}\right)^2}{\left(1 + \frac{2363\,Cu}{mPV}\right)\left(B + \frac{h}{s} + p\right)}.$$

The discrepancy between the two coefficients 2363 and 2358.5 must be due to the fact that Gaus used for the atomic weight of copper a value other than 63.6. Further differences between the two formulas are caused by Gaus leaving out the volume of the water vapor in the right-hand member of the equation on p. 244, 11th line from above. With this correction introduced, his formula becomes identical with that given above. The two equations, however, give as they stand only slightly differing values for the vapor-pressure of the ammonia. The chief advantage of that derived by us consists in its much simpler form.

The corrections for the reduction of the barometric readings to 0° (B_0) were taken from Landolt and Börnstein's tables, p. 35.

The hydrochloric acid was prepared from sodium chloride and sulphuric acid, both chemically pure. The gas was received in water, the conductivity of which lay between 2×10^{-6} and 1.6×10^{-6}, and the acid used in the experiments was prepared from this supply by dilution with some of the same water. The acid in the resistance cell was approximately 0.01 normal, its exact strength being determined by its conductivity. For this purpose the conductivity for $\frac{1}{256}$,

[1] Ztschr. anorg. Chem., 25, 244.

$\frac{1}{128}$, and $\frac{1}{64}$-normal acid at 25°, as given by Kohlrausch and Holborn (Leitvermögen der Elektrolyte, S. 167), were employed. The coefficients of a parabola passing through these three points and the origin were first calculated. This parabola, which probably coincides very closely within these limits, with the actual curve showing the relation of conductivity to concentration, has the formula

$$m = 2.5575k + 0.000146p - \frac{\sqrt{2.1316 + 3136.6k}}{10000}, \quad \text{(III.)}$$

where m is the concentration and k the corresponding conductivity.

This equation gives the strength of the acid at 18°. The acid being very dilute, we used as a correction in converting this value into normality at 25° merely the expansion of water alone for the same interval. The volume of the acid was measured in a specially constructed pipette (Fig. II.), which at 25° held 14.26 cc. This pipette was completely filled with the acid and then hung in the thermostat, with its mouth protected by a small tube and the cock closed. We were by this means always sure to use exactly the same volume of acid, independently of the temperature of the room.

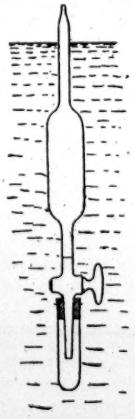


Fig. II.

The degree to which the acid is neutralized by the ammonia carried over, or P, is calculated from the conductivity, first of the pure acid and then of the partially neutralized solution. The experiment was allowed to proceed only until 70 to 80 per cent of the acid was neutralized, to avoid all possibility of some ammonia escaping absorption. As a check in this regard, a second receiver containing acid was occasionally attached to the cell. When the experiments were carried on as above, the conductivity of the acid in this second cell remained absolutely unchanged.

In order to determine the relation between the conductivity of the acid and the degree to which it was neutralized by ammonia, Gaus merely measured the conductivity of the former at stated intervals during the course of an experiment. He gives no data, but assumed from his results that the fall in conductivity was directly proportional to the amount of ammonium chloride formed. This relation, of course, is the very basis upon which all the experimental data depend. As the resistance is constantly increasing throughout the experiment, and owing to the fact that the change occurs, not uniformly, but in abrupt steps as the successive bubbles of gas enter the resistance cell, it seemed to us that this method was, to some degree, open to criticism. We ventured, therefore, to control his results by measuring the conductivity of an acid to which known quantities of ammonia had been added. To this end, a definite volume of acid was measured off, mixed with a known amount of ammonia which had been standardized against it, and after dilution to the proper extent the conductivity of the solution, at 25°, was determined. That of the acid alone, under the same conditions, was 0.004097, corresponding to an 0.01024 normal solution. The various measurements made are given in Table II.

Table II.

k.	P. Per cent.	P. cals. Per cent.	D. Per cent.
0.004097	0.00	—2.62	—2.62
0.002146	72.08	[72.08]	....
0.002100	73.89	73.84	—0.05
0.002047	75.90	75.87	—0.03
0.001927	80.42	80.46	+0.04
0.001703	89.04	[89.04]	....
0.001420	100.00	99.88	—0.12

Under P cals. are given the theoretical percentages of ammonium chloride required on the assumption that between P = 72.08 per cent and P = 89.04 per cent the conductivity curve is rectangular. Between these two values the coincidence is actually very good indeed. The equation of this line, which is

$$P = 154.24 - 38285k, \qquad (IV.)$$

does not give a value for P when $k = 0.004097$ ($P = 0$) and is not very satisfactory for $k = 0.00142$ ($P = 100$). Although between the extremes in our experiments the equation holds good and can be used for the calculation of the degree of neutralization, therefore, it seems that Gaus' assumption is not wholly true.

In order to avoid the tedious necessity of preparing at intervals during the investigation a new acid solution of exactly the same conductivity as the above, a supply of about 2 liters was made, as occasion required, which had as nearly as possible the same concentration, and the value of P corresponding to the final conductivity was then subjected to a simple correction. To calculate the latter, the assumption was made that for very slight intervals of concentration the conductivity is directly proportional to the normality. While this is, of course, not true within wider limits, the error which it involves in our experiments may be entirely neglected. The limits of conductivity of all the acids used were 0.004097 and 0.004068. According to equation III., these figures correspond to the concentrations 0.010239 and 0.010164, respectively. On the basis of the above assumption the normality of the second acid would be $\frac{406.8}{409.7} \cdot 0.010239$, or 0.010167. The difference between this value and 0.010164 is without significance for our purpose. Under the same conditions, the same assumption may be made in regard to an ammonium chloride solution.

If two acid solutions, of the molecular concentrations n_1 and n_3, and conductivities k_1 and k_3, respectively, be gradually neutralized by ammonia until they have become ammonium chloride solutions with the conductivities k_2 and k_4, the curves representing the involved changes of conductivity may be represented by I. and II., in Fig. III. Let k''_P be the conductivity of the second acid, measured after it has been neutralized to P per cent by ammonia, and the corresponding, as yet unknown, conductivity of acid I. be k'_P. The two curves are not exactly parallel, but when the range of concentration of

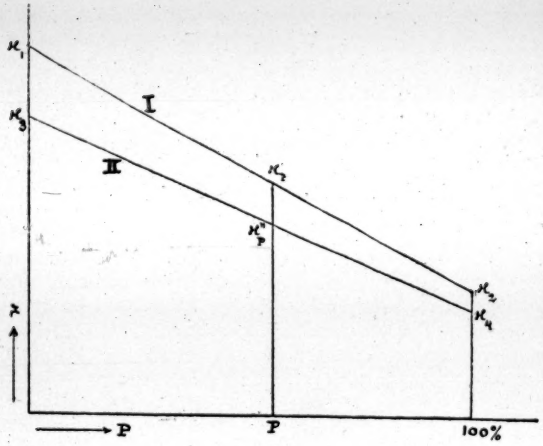


Fig. III.

the acids is very slight, they become approximately so, and their eccentricity is in the same direction. No noticeable error is introduced, therefore, in assuming the equation

$$k'_P = \frac{k''_P}{k_3} . k_1 .$$

If we designate the resistance capacity of the cell by C, and the resistances corresponding to the measured conductivities k_3 and k''_P, by W_1 and W_P, respectively, then $k''_P = \frac{C}{W_P}$ and $k_3 = \frac{C}{W_1}$, whence,

$$k'_P = \frac{W_1}{W_P} k .$$

By this equation the conductivity of an acid solution of the original conductivity $k = 0.004097$, which has been neutralized to very nearly the same degree, can be calculated, and from this value the wished-for percentage of saturation estimated by (III.).

The investigated ammoniacal copper solutions were prepared as follows: A pipette, of the construction shown in Fig. II., was filled, at 25°, from a supply of copper sulphate solution, the strength of which had been very accurately ascertained. This solution was run into a measuring-flask, and a measured quantity of a stock solution of ammonia then added from a calibrated burette. The proper quantity of water was then added and the temperature noted. The concentration of the ammonia was determined volumetrically, in a second portion of the stock solution, whenever a fresh mixture was prepared. The ammonia solutions used were prepared from the purest ammonium chloride and calcium hydroxide.

The normality of the total ammonia in the cupric solutions at 25° was calculated from the temperature of the solutions when prepared, and the expansion coefficients of the glass, the ammonia solution, and of the hydrochloric acid by which the latter was standardized. The expansion of the cupric ammoniacal solution was assumed to be the same as that of a pure ammonia solution of the same concentration. The correction for hydrochloric acid was obtained by interpolation between the values given by Schulze[1] for the normal acid and pure water. For the ammonia, the tables of Lunge and Wiernik[2] were used.

Experimental Results and Conclusions.

The first series of experiments was directed toward the question as to how far water solutions of ammonia follow Henry's law. Gaus assumed, from results of three experiments, which agreed only approximately with the theoretical, that the ratio between concentration and vapor-pressure of the ammonia is constant. The vapor-pressure was determined by us for five concentrations, varying from about 0.01 to 1 gram-molecule per liter. These preliminary results are given in Table III., and their graphic presentation in Curve I., Fig. IV.

[1] Ztschr. anal. Chem., 21, 167.
[2] Ztschr. angew. Chem., 1889, 183.

Table III.

Molecular strength = n.	P_2. mm.	P_2 mean.	P_2 calculated.	Difference.
0.096	1.30	1.29	1.30	+0.01
"	1.27	....	....	....
0.242	3.25	3.23	2.27	+0.04
"	3.21	....	....	....
0.406	5.41	5.41	5.49	+0.08
"	5.41	....	....	....
0.729	9.80	9.80	9.86	+0.06
0.993	13.42	13.42	13.42	0.00
"	13.42	....	....	....

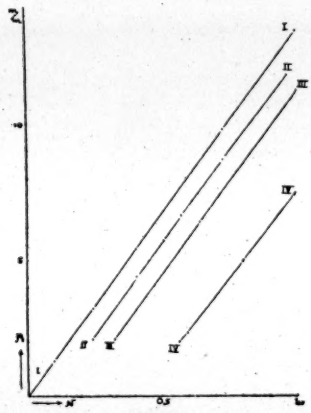


Fig. IV.

The equation of the line passing through the origin and the point $P_2 = 3.42$, $n = 0.993$ (Fig. IV.), is

$$P_2 = 13.52n.$$

The pressures at lower concentrations, as shown in the above table, are very considerably below the values calculated from this formula. The agreement is, nevertheless, much closer than was found by Gaus, as is seen from the following, in

which the theoretical values are calculated from his formula, $P = 13.45n$.

n.	P_3.	Calculated.	Difference.
1.00	13.45	13.45	0.00
0.902	9.35	9.44	+0.09
0.456	5.97	6.13	+0.16

There can be no doubt, however, but that the law does not hold strictly true. Our own results are expressed somewhat more exactly by the quadratic equation

$$P_3 = 0.18n^2 + 13.34n, \qquad (V.)$$

from which the following values are obtained :

n	0.096	0.242	0.406	0.729	0.993
P_3	1.28	3.22	5.44	9.82	13.42
D	−0.01	−0.01	+0.03	+0.02	0.00

In the experiments on solutions containing copper, the highest concentration of ammonia was, with one exception, 0.963 normal. The residual ammonia in these solutions, a certain amount having been taken up to form the complex salt, is much less than the original quantity, and in fact rarely exceeded 0.70 normal. For ammonia solutions of concentration less than this, down to the lowest with which we experimented, we can disregard this slight variation from the law. Between these limits the equation

$$P_3 = 13.42n$$

gives very excellent results :

Table IV.

n.	P_3 calculated.	Difference.
0.096	1.29	0.00
0.242	3.25	+0.02
0.406	5.45	+0.04
0.729	9.78	−0.02

The variations here are only very slightly greater than when the above quadratic equation is employed. For the sake of showing more distinctly a certain parallelism between the curves of the vapor-pressure of ammonia in water alone and in presence of cupric sulphate, therefore, we have adopted

as the means of determining the concentration of the residual ammonia in the salt solutions the relation

$$P_3 = 13.42n.$$

The formula used for this purpose, accordingly, is

$$n_1 = \frac{P_3}{13.42},$$

n_1 being the concentration of the residual ammonia.

Ammoniacal Copper Solutions.—Experiments were made in two directions, the first being to ascertain how far the ratio of combined ammonia (n—n_1) to copper varies with varying quantities of ammonia and a constant amount of copper, and the second, to find out the effect of varying concentration of the salt.

In the first series, a solution containing 0.0235 gram-molecule of copper sulphate was chosen, the ammonia varying in different experiments from a quantity barely sufficient to redissolve the cupric hydroxide at first formed, up to an approximately normal solution, in which the ratio of copper to total ammonia is about 1 : 40. Table V. contains the results, to which the curves II–II, Fig. IV., correspond.

Table V.—Cu = 0.0235.

n.	P_3 ohms.	Mean.	P_3 calculated.	Difference.
0.239	2.12	2.12	2.12	0.00
0.406	4.38	4.41	4.37	—0.04
"	4.44	....	....	....
0.508	5.72	5.73	5.73	0.00
"	5.73	....	....	....
0.575	6.65	6.66	6.63	—0.03
"	6.67	....	....	....
0.730	8.71	8.71	8.71	0.00
0.963	11.80	11.80	11.84	10.04

The vapor-pressure of the ammonia in these solutions is apparently very nearly directly proportional to its concentration. The calculated values for P_3 were obtained from the mean linear equation

$$P_3 = 13.41n - 1.08.$$

Now the curve of this equation is practically parallel to that

exerted in the more dilute aqueous solutions of ammonia alone. The difference between the two coefficients of n, 13.42 and 13.41, is hardly to be controlled by experiment. This indicates that, at least for concentrations of ammonia lying between 0.239 and 0.730 normal, the decrease in the pressure of ammonia, and consequently the amount of ammonia which has passed into combination with the copper, is constant for this concentration of the copper sulphate.

The following table gives the quantity of residual and combined ammonia in the various solutions. These values were calculated from the above mean equations:

Table VI.

n.	Cu : n.	n_1.	Cu : n_1.	Combined NH_3 $(n-n_1)$.
0.239	1 : 10.17	0.158	1 : 6.72	0.081
0.406	1 : 17.26	0.325	1 : 13.83	0.081
0.508	1 : 21.62	0.427	1 : 18.17	0.081
0.575	1 : 24.47	0.494	1 : 21.02	0.081
0.730	1 : 31.06	0.649	1 : 27.62	0.081
0.963	1 : 40.98	0.882	1 : 37.53	0.081

For ammonia of the concentration 0.882, the linear equation $P_s = 13.42n$ is not strictly applicable, using the quadratic equation, the residual concentration, n, becomes in this case 0.879, and the combined, 0.084. In the other experiments, the combined ammonia when calculated by this equation ranges from 0.080, in the first, to 0.082, when $n = 0.730$. This very slight increase in the amount of combined ammonia is practically within the limit of error, but will be discussed at a later point.

The combined ammonia, 0.081 gram-molecule, stands to the copper in the ratio of 3.45 : 1. The fact that this molecular ratio remains constant even when the ratio of copper to total ammonia varies from 1 : 10 to 1 : 30, does not conform with Dawson and McCrae's observations. With virtually the same concentration of copper (Table I.) they found a variation of from 1 : 3.14, when Cu : total ammonia = 1 : 6 to 1 : 3.96, when Cu : total ammonia 1 : 16. We have found it impossible, however, to prepare a solution containing this amount of copper and only 6 molecules of ammonia. Solutions may

readily be prepared which are apparently clear, but after some time they deposit a dark-green, amorphous precipitate, which clings to the sides of the vessel, and is probably a highly basic salt. The amount of copper thus removed from the solution was in one case quantitatively determined. For this purpose, a solution containing 0.0235 gram-molecule copper and 0.1513 N ammonia, corresponding to the molecular ratio $Cu : NH_3 = 1 : 6.45$, was steadily shaken for two days at 25°. On removal from the thermostat at the end of that time, a very considerable precipitate had formed. This was filtered off and the normality of the filtrate, with respect to copper, was determined in an aliquot portion. It proved to be only 0.0123 molecular, representing a loss of nearly 50 per cent by precipitation. Even when the ratio of $Cu : NH_3$ was 1 : 10, evidence of slight double decomposition was obtained. The solution used in the first experiment (Table V.) showed with time a marked decrease in the vapor pressure of its ammonia. When freshly prepared, it gave for P_3 the value 2.12 mm., on the next day 2.05 mm., and on the third 1.98 mm. This can be explained only by the assumption that a soluble, or colloidal, basic salt and ammonium sulphate were gradually being formed.

The most probable complex formed by cupric copper and ammonia is certainly $Cu(NH_3)_4^{++}$. This is indicated by practically all experiments hitherto made in investigation of the subject. The fact that the amount of ammonia actually found to have passed into combination falls short of the amount which is required for the formation of this complex cannot be explained by the assumption that the solution contains two complexes, such as $Cu(NH_3)_4^{++}$ and $Cu(NH_3)_2^{++}$. In that case we could hardly expect the actual molecular ratio to be practically independent of the concentration of the residual ammonia. That it is so, our results very decidedly indicate. The assumption that the complex formed is $Cu_3(NH_3)_7^{++++}$, which would correspond roughly with the observed ratio, $Cu : NH_3 = 1 : 3.45$, is also hardly permissible, especially in the light of our subsequent experiments. If, then, the only complex formed is $Cu(NH_3)_4^{++}$, we must look

to physical causes to account for the very considerable difference between the observed decrease in the vapor-pressure of the ammonia and that which is calculated for the formation of this compound. The most plausible explanation, we believe, is found in the decreased solubility of ammonia in a solution of the complex copper salt, as compared with its solubility in water. If this be true, the vapor-pressure of the residual ammonia in the cupric solution would be higher than that of the same amount in water, and the calculation of the residual ammonia by the formula

$$n_1 = \frac{P_1}{13.42}$$

accordingly yield results which are too high. This assumption is thoroughly in accord with the experiments hereafter to be described.

Assuming that 4 molecules of ammonia combine with 1 of copper, and that the amount of unaltered cupric ions, or of copper sulphate, is inappreciable, the difference between this quantity and that found by the vapor-pressure, as above, is 0.0235 (4.0—3.45), or 0.0129 gram-molecule per liter. This seems, at first glance, to be very great, compared with the concentration of the copper, but in reality it is about what we should expect. The resemblance between the complex metal-ammonia compounds and the salts of the alkali metals is in many respects very striking. As has previously been stated, Gaus found that the addition of 0.4 molecule of potassium chloride to a normal solution of ammonia caused an increase in the pressure of the latter about equal to the vapor-pressure of 0.075 N. ammonia. If we calculate from these data, by Jahn's formula,[1]

$$\frac{S-S_1}{M^{2/3}} = k,$$

the effect of 0.0235 molecule potassium chloride, the result is almost the same as in the cupric solution, 0.012 gram-molecule as compared with 0.0129 gram-molecule. In this formula, S is the solubility of the gas in the pure solvent, S_1 its

[1] Ztschr. phys. Chem., 18, 8 (1895).

solubility in the solution, and M the concentration of the dissolved salt.

By means of this formula we can find an approximate correction by which to obtain the true concentration of the residual ammonia, n_2. The constant k, which is given by the data of the above experiments, has the value 0.1588. For any concentration of copper, therefore,

$$+n_1 - n_2 = 0.1588M^{2/3},$$

in which n_2 is the true concentration. We have then,

$$n_2 = \frac{P_2}{13.42} - 0.1588M^{2/3}.$$

In solutions containing twice as much copper sulphate as was used in this series of experiments, or 0.047 molecule, this correction amounts to 0.021. The observed ratio of copper to combined ammonia should, therefore, be approximately $1 : 4 - \frac{0.021}{0.047}$, or 1 : 3.55. This was confirmed by the following experimental results:

Table VII. Cu = 0.047.

n.	P_2.	Mean.	P_2 calculated.	Difference.
0.322	2.13	2.11	2.11	0.00
"	2.11	....	....	....
"	2.09	....	....	....
0.644	6.43	6.41	6.43	+0.02
"	6.39	....	....	....
1.000	11.25	11.23	11.21	—0.02
"	11.25	....	....	....

As would be expected from the above, we again find the decrease in vapor-pressure independent of the concentration of the ammonia. Under P_2 calculated stand the values derived from the mean equation

$$P_2 = 13.42n - 2.21,$$

the curve of which (III.—III., Fig. IV.), runs parallel to those obtained in the previous experiments

NH_3. $P_2 = 13.42n$;

$Cu = 0.0235$. $P_2 = 13.41n - 1.08$.

The results of this series of experiments, in respect to the amount of residual ammonia found, etc., are given in Table VIII. :

Table VIII.

n.	Cu : n.	n_1.	Cu : n_1.	$n-n_1$.
0.322	1 : 6.85	0.157	1 : 3.34	0.165
0.644	1 : 13.70	0.479	1 : 10.19	0.165
1.000	1 : 21.28	0.835	1 : 17.77	0.165

If the variation from Henry's law by ammonia be taken into consideration the residual ammonia, n_1, becomes respectively 0.158, 0.478, and 0.834, figures which differ only very slightly from the above. The molecular ratio of copper to combined ammonia, $\frac{n-n_1}{\text{Cu}}$, comes to 1 : 3.51, and the difference between this and 1 : 4, or 0.49 molecule ammonia, represents a concentration of 0.023 molecule per liter—the correction due to increased solubility in the salt solution. This agrees very closely with the calculated value for this correction, 0.021 molecule. Using the latter, we have for n_1 the value 0.186, and the molecular ratio $\text{Cu} : \text{NH}_3 = 1 : 3.96$.

These experiments, to a certain extent, confirm Gaus' conclusion that the lowering of the vapor-pressure of the ammonia by the addition of copper sulphate is directly proportional to the amount of the latter added. In our two experiments, the decrease is 1.08 mm. for 0.0235 Cu, and very slightly more than twice this amount, or 2.21 mm. for 0.047 Cu. Gaus found the decrease to be 2.49 mm. for 0.0491 Cu, and 5.02 mm. for 0.0982 Cu. His molecular ratios, 1 : 3.77 and 1 : 3.80, however, are somewhat higher than those observed by us.

In the next, and last, series of experiments the amount of copper sulphate added was five times as great as in the first series, or 0.1175 molecule. According to Jahn's formula, the decrease in the solubility should in this case be 0.038 gram-molecule, corresponding to 0.32 molecule copper. The observed ratio of copper to combined ammonia should, therefore, be $1 : 4 - 0.32$, or 1 : 3.68. The experimental data are as follows :

Table IX. $Cu = 0.1175$.

n.	P_2.	Mean.	P_2 calculated.	Difference.
(0.564	(2.02	(2.01)	....	....
"	1.99)	....	....	....
0.596	2.35	2.33	2.38	—0.02
"	2.33	....	....	....
"	2.32	....	....	....
0.803	4.98	4.96	4.98	+0.02
"	4.94	....	....	....
0.804	5.03	5.02	5.00	—0.02
"	5.02	....	....	....
"	5.01	....	....	....
0.993	7.43	7.42	7.44	+0.02
"	7.44	....	....	....
"	7.38	....	....	....
0.995	7.50	7.48	7.46	—0.02
"	7.48	....	....	....
"	7.47	....	....	....
"	7.46	....	....	....

As in the previous series, the pressure is directly proportional to the concentration of the ammonia. The ratio of copper to combined ammonia, in these more concentrated solutions, however, is no longer quite constant, the mean equation of the pressure curve (IV.–IV., Fig. IV.), being

$$P_2 = 12.91n - 5.38.$$

This equation satisfies the above values of P_2 for all concentrations of ammonia except the first, 0.564. In this case the amount of residual ammonia, as compared with the copper, is far lower than in any previous instance, and it is probable that a basic salt had formed to a slight extent. The difference between the observed and calculated values of P_2 for this concentration was 0.11 mm. A solution containing less ammonia could not be prepared at all. Table X. contains the data calculated from the results of the other experiments.

Table X. $Cu = 11.75$.

n.	Cu : n.	n_1.	Cu : n_1.	$n - n_1$.	$\frac{n - n_1}{Cu}$.
0.596	1 : 5.07	0.171	1 : 1.46	0.425	3.62
0.803	1 : 6.83	0.371	1 : 3.16	0.432	3.68
0.804	1 : 6.84	0.372	1 : 3.17	0.432	3.68
0.993	1 : 8.45	0.554	1 : 4.71	0.439	3.73
0.995	1 : 8.47	0.556	1 : 4.73	0.439	3.73

Corrected for decreased solubility, the combined ammonia, $n - n_s$, and the molecular ratio $\frac{n-n}{Cu}$, become

$n - n_s$.	$\frac{n-n_s}{Cu}$.
0.463	3.94
0.470	4.00
0.470	4.00
0.477	4.05
0.477	4.05

The coincidence between these results and the theoretical is in general very good indeed. It cannot be doubted, however, but that the molecular ratio is not quite constant in these solutions in which the concentration of the copper is relatively great. The difference between the values found for the concentration of the residual ammonia in the first and last experiments, 0.014 molecule, is well outside the error of experiment, as it represents a vapor-pressure of 0.2 mm. We are disposed to ascribe this increase in the amount of combined ammonia to the formation, in a slight degree, of a higher complex, $Cu(NH_3)_6^{++}$ or $Cu(NH_3)_6^{++}$. The same phenomenon probably occurs, though only to a negligible extent, in the solutions which contain less copper, and this may be the cause of the slight increase in the molecular ratio observed, in the first series of experiments (Table VI.), in the solution containing 0.963 N. ammonia.

Even in the more concentrated solutions of this series the amount of the higher complex formed with 0.9905 N. ammonia is insignificant. If we assume its formula to be $Cu(NH_3)_6^{++}$, the increase in the molecular ratio from 1 : 3.94 to 1 : 4.05 means the passage of only 0.0035 gram-molecule, or about 3 per cent, of the copper into the higher complex. Whether the quantity formed is really directly proportional to the excess of ammonia, or not, cannot, of course, be determined in solutions of this strength, the concentration of the higher complex being too low. The investigation of more concentrated cupric solutions would probably throw at least enough light on the subject to tell us whether the second complex has

the formula $Cu(NH_3)_5^{++}$ or $Cu(NH_3)_6^{++}$. We regret that through an unfortunate circumstance we have been obliged to forego further research on the subject. It seems, probable, however, that $Cu(NH_3)_6^{++}$ is the compound more likely to result. This is indicated by the behavior of salts of nickel, so close an analogue of copper. A large number of nickel salts derived from the complex $Ni(NH_3)_6^{++}$ are known in the solid state, and can be crystallized from ammoniacal solutions, although Dawson and McCrae found that in nickel solutions, as in those of copper, less than 4 molecules of ammonia are absorbed to 1 of the metal.

The above experiments have been described in the order in which they were performed. For the sake of convenience in the development, therefore, the correction due to the decrease in the solubility of ammonia in water upon addition of cupric sulphate, was calculated from the results of the first series alone. The value assigned to it, as judged by the data of the subsequent experiments, is probably somewhat too low. Using the data of the second series, $Cu : NH_3 = 1 : 3.51$, as the basis of the calculation, we obtain

$$n_2 - n_1 = 0.1768M^{2/3}.$$

The mean between this coefficient and that which was used, 0.1588, is 0.1678, and this is probably very nearly correct. For the molecular ratio in the first two series, and in the first experiment in the third series, in which the observed ratio was the lowest, it yields:

$Cu = 0.0235$	$Cu : NH_3 = 1 : 4.03$
$Cu = 0.0470$	$Cu : NH_3 = 1 : 3.98$
$Cu = 0.1175$	$Cu : NH_3 = 1 : 3.95$

This coincidence satisfies the requirements of the theory advanced very well indeed.

Summary.

1. The molecular ratios between the copper and amount of combined ammonia in ammoniacal copper sulphate solutions, found by Dawson and McCrae, and others, can be explained only by one or two assumptions. Either two com-

plexes result or the difference between the ratio Cu : $4NH_3$ and the observed ratio is due to the fact that the methods employed do not give the correct values for the residual concentrations of ammonia.

2. This second assumption is probably the true one. When the concentration of copper is low, the amount of ammonia which enters into combination, and hence the molecular ratio, is constant. For Cu = 0.0235, the ratio 1Cu = 3.45 NH_3 was found; for Cu = 0.0470, the ratio was 1Cu = 3.51 NH_3. This held true for all concentrations of ammonia between 0.239 and 0.729 molar in the first case and 0.322 and 1.000 molar in the second. This can be explained only on the theory that ammonia is less soluble in cupric sulphate solutions than in water, in which case the observed vapor-pressure in the salt solution gives too high values for the concentrations of the residual ammonia. The correction involved was calculated by Jahn's formula and found to equal $0.1678M^{2/3}$, where M is the molecular concentration of the copper. Its value is about the same as that for ammonia in solutions of potassium chloride. With this correction the ratios in the two series become respectively

$$Cu : NH_3 = 1 : 4.03 \quad \text{and} \quad Cu : NH_3 = 1 : 3.98.$$

It must be assumed, therefore, that in solutions of this concentration all the copper passes into the complex $Cu(NH_3)_4^{++}$.

3. In solutions where the concentration of the cupric sulphate is 0.1175 molar, the same relation holds true when the excess of ammonia is not very high. The observed ratio of copper to combined ammonia was then 1 : 3.62, and the corrected ratio 1 : 3.95. With higher concentrations of the ammonia a small quantity of a higher complex, $Cu(NH_3)_5^{++}$ or $Cu(NH_3)_6^{++}$, forms, this amounting to about 3 per cent of the total copper when the concentration of ammonia is about normal.

Dr. Forssall's services were secured to me for the foregoing investigation through the generosity of the trustees of the Austin Fund of the Massachusetts Institute of Technology, who placed a very liberal grant at my disposal with which to

carry out the research. I wish to express to them my thorough appreciation of their assistance. J. L.

MASS. INSTITUTE OF TECHNOLOGY,
BOSTON, MASS., July, 1903.

REVIEWS.

JOURNAL DE CHIMIE PHYSIQUE: ELECTROCHIMIE, THERMOCHIMIE, RADIOCHIMIE, MÉCANIQUE CHIMIQUE, STOECHIOMÉTRIE. Publie par M. PHILIPPE A. GUYE, Professeur de Chimie à l'Université de Genève.

The appearance of this new journal of physical chemistry in French will undoubtedly mark a new epoch for this subject in France. Certain chapters in physical chemistry owe their existence largely to the work of French chemists. We should mention especially the work of Raoult on the lowering of the freezing-point and vapor-tension of solvents by dissolved substances, that of Berthelot on thermochemistry, of Pasteur on optical activity, of Guye on the effect of changing the masses of the atoms or groups on optical activity, of Le Chatelier on chemical equilibrium, and many other investigations of great importance to physical chemistry have come from those who read most easily the French language.

The present journal will bring the subject as a whole more closely home to the French chemists, and we may fairly expect from them renewed activity in this field.

Prof. Guye can be heartily congratulated upon his efforts to establish the new journal, which we hope may prove to be an honor to its subject, as well as to its country and editor.

H. C. J.

A PHYSICO-CHEMICAL REVIEW. A Complete International Review of the Sciences of Physical Chemistry, and the Allied Branches of Chemistry and Physics. Edited by DR. MAX RUDOLPHI, Darmstadt.

The journal in question is not to be an organ for the final publication of original investigations, but a "comprehensive, centralizing review of progress in physical chemistry." The journal is to be distinctively international in character, and is to include English, French, and German abstracts. It is the desire of the editor that the abstracts should be prepared, whenever possible, by the authors of the papers, and will be published immediately after the publication in other journals of the original papers. The journal aims to cover the entire field of general or physical chemistry, and also to include those publications in chemistry and physics which have any physical chemical bearing.

It is obvious from this sketch that the new "Review" aims to bring physical chemical literature together in a manner not done at present by any other journal. It will doubtless contribute its share to the development of this growing branch of science, and we wish it the very best success. H. C. J.

QUANTITATIVE CHEMICAL ANALYSIS. Adapted for use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc., London, Emeritus Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, A.R.C.Sc., Dublin, Professor of Chemistry in the Southwestern Polytechnic, Chelsea, S. W. Sixth Edition. Philadelphia: F. Blakiston's Son & Co. 1903. pp. xxiv + 602. Price, $3.50 net.

The present edition differs from that issued in 1900 by the addition to the appendix of a description of the procedure of Landsberger, as modified by Walker and Lumsden, for the determination of molecular weights by the rise of boiling-point of solutions, a procedure for the analysis of aluminium alloys, a description of the Soxhlet condenser, and a table of four-place logarithms. The description of the estimation of cyanide by means of iodine is omitted. The authors state that the entire text has been subjected to revision. This, however, apparently relates to minor details, with the exception of the changes above noted.

The subject-matter of the volume is well arranged for teaching purposes and is indexed with unusual care and thoroughness. The statements regarding preliminary operations and the pre-requisites for successful quantitative work are forceful and clear. These are followed by descriptions of a considerable variety of gravimetric determinations, including about forty elements or radicals. Typical volumetric processes are the subject of the third large division of the book, while in Part IV. both gravimetric and volumetric processes are applied to a wide range of materials of technical importance, to methods of analysis of waters, food-stuffs, soaps, and tanning materials, and to methods of ultimate organic analysis. Part V. deals with the analysis of gases, Part VI. contains tables for reference, and Part VII. and the appendix include supplementary information useful for the analyst.

It is difficult to properly define the scope of a manual of quantitative analysis after it has passed the bounds of an introductory treatise. The authors, in this instance, have avowedly limited themselves to the presentation of procedures which have given satisfactory results in their laboratories, and they have also appended a list of works of reference upon general and special lines of analysis. This, of course, largely disarms criticism of their selection of methods since it is im-

possible to determine to what extent the pupil is made to understand that he should, in his post-graduate experiences, look about for other methods than those given in this volume before making a final choice of procedure for his work in hand. Yet one cannot help wondering, for instance, why, when so much is said of the color-test for the determination of carbon in irons and steels, no mention is made of the color-test for manganese, or of the rapid volumetric methods for manganese or phosphorus among methods which are represented as typical of those in general use for the analysis of this class of material. The absence of the Lunge method for the determination of sulphur in pyrites is also noteworthy.

The list of works and journals for reference is restricted to those in English, and essentially to those published in England. As the average student has too strong a tendency, at best, to confine his reading to his own language and country, and to feel that time devoted to the acquisition of a foreign language is but ill-spent, the entire omission of reference to works in French or German (and possibly to American chemical journals as well) seems to foster that tendency.

No reference is made to the ionic theory of its applications, and the statements of the principles underlying the vapor-density determinations are very brief.

Whatever differences of opinion may, and inevitably will, be held regarding the selection of individual methods of analysis, the fact that the present is the sixth edition of this work in twelve years is adequate indication that it has deservedly made many friends. H. P. T.

DIE KONSTITUTION DES KAMPHERS UND SEINER WICHTIGSTEN DERIVATE. Die theoretischen Ergebnisse der Kampherforschung monographisch dargestellt von OSSIAN ASCHAN. Verlag von Fr. Vieweg und Sohn, Braunschweig. One vol., pp. xi + 117. 1903. M. 3.50.

Camphor is one of the first chemical individuals of an organic nature known to chemists. Its medical, ritualistic, and commercial history added to the interest of this natural product from the Orient. It, therefore, attracted the attention of chemists even before organic chemistry began to develop as a distinct branch of our science. It even gave its name to an entire group of natural and artificial compounds, yet for more than a hundred years its own molecule remained a mystery to the investigators of all civilized countries who tried to unravel its constitution. In recent decades, chemists not especially engaged in the study of camphor and its derivatives could no longer hope to follow the work of the small army of investigators in this field. The monograph of Aschan, therefore, will

be very welcome to all who desire light on this interesting subject.

After a brief historical introduction, the author discusses not less than thirty-three structural formulas proposed for camphor. He then presents twelve definite structural conclusions based on experiment which bear upon the arrangement of the atoms in the camphor molecule. In a fourth chapter he submits the camphor formulas, presented in the second chapter, to a careful scrutiny in the light of these twelve corollaries, as they may be called, and comes to the conclusion that the Bredt formula alone is in harmony with all, while it is the only one which admits of a satisfactory explanation of the conversion of camphor to symmetrical camphene. The keystone of this arch of corollaries, the satisfactory synthesis of camphor, is still wanting.

The remaining chapters are devoted to further "Abbau" products of camphor and to the constitution of camphene and bornylene.

Aschan's monograph is certainly a unique volume in modern chemical literature. The author has done well to exclude all descriptions of substances and processes from this speculative account. These are to be included in a larger work covering all alicyclic compounds, soon to be published. E. K.

THERMODYNAMICS AND CHEMISTRY. A Non-mathematical Treatise for Chemists and Students of Chemistry. By P. DUHEM, Correspondant de l'Institut de France, Professor of Theoretical Physics at the University of Bordeaux. Authorized translation by GEORGE R. BURGESS, Docteur de l'Université de Paris, Instructor in Physics, University of California. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1903. pp. 445.

The author is greatly impressed with the importance of thermodynamics for the chemist. This is seen from his own words taken from his preface: "The laws formulated by thermodynamics impose a rational order upon the most confused chapters of chemistry; a few simple, clear rules bring order out of what was a chaos; the circumstances under which the various reactions are produced, the conditions which stop them and assure chemical equilibrium, are fixed by theorems of a geometrical precision." "What the chemist expects above all from thermodynamics are simple, clear rules, easy to use, which shall serve him as conducting threads through the fruitful labyrinth of chemical facts already known, which shall guide him in the course of his researches, which shall show him exactly, for every reaction, the variable conditions at his disposal and the essential conditions which he is held to determine."

The author is greatly impressed with the depth and value of the work of that distinguished American physicist, J. Willard Gibbs, and his work shows the imprint of this master at every stage.

The contents of this excellent book can be judged best by a brief reference to the headings of the twenty chapters of which it is composed. They are: Work and Energy, Quantity of Heat and Internal Energy, Chemical Colorimetry, Chemical Equilibrium and the Reversible Transformation, The Principles of Chemical Statics, The Phase Rule, Multivariant Systems, Monovariant Systems, Multiple or Transition Points, Displacement of Equilibrium, Bivariant Systems—The Indifferent Point, Mixed Crystals—Isomorphous Mixtures, Critical States, Chemical Mechanics of Perfect Gases, Capillary Actions and Apparent False Equilibrium, Genuine False Equilibrium, Unequally Heated Spaces and Chemical Dynamics and Explosions.

The work as a whole may be said to be a sign of the times, and an indication of what the chemistry of the future will be. Every such contribution to the literature as the one in hand will contribute to this end.

The work of the translator seems to have been faithfully done. The only fault that we can find is that the translation is in places too literal. In the preface we find such statements as "this opposition has been *exposed* with very great clearness," "the work in which I have tried to *expose*, etc," "we have accompanied each of them with numerous examples." These are, after all, comparatively small matters, and any one who has any appreciation of the drudgery involved in translating a work of any size will feel thankful to Dr. Burgess for making this book accessible to English-speaking students. It is to be hoped that the book will receive the attention that it deserves.

H. C. J.